IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN THE APPLICATION OF: CONFIRMATION NO.   9545

DONALD L. RYMER ET. AL.   CASE NO.:   AD6856 US PCT

SERIAL NO.:   10/501,598   GROUP ART UNIT: 1796

FILED: JULY 13, 2004   EXAMINER: WILLIAM K. CHEUNG

FOR: LOW-COLOR PVB SHEET AND A PROCESS FOR MAKING SAME

DECLARATION UNDER 37 CFR1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Donald L. Rymer, declare and state:

I am a named co-inventor on the subject patent application and am an employee of E. I. du Pont de Nemours and Company (DuPont), the assignee of the subject patent application.

In 1966 I was awarded a Bachelor of Science degree in Chemistry from Salem College.

In 1968, I was awarded a Master of Science degree in Organic Chemistry from Ohio University in Athens, Ohio.

I have worked for DuPont for over 39 years in a variety of manufacturing technology and research assignments.

I am currently a Technology Fellow conducting product and process research for the Packaging and Industrial Polymers (P&IP) business and work in the field of poly (vinyl butyral) (PVB).

I have worked in the PVB field for over 30 years developing polymer syntheses, troubleshooting manufacturing problems, and improving our product as it is incorporated as an interlayer in glass laminates.

I have been a lead technology person in starting up PVB labs and processes outside the U.S. and continue to be involved in the design of new products.

I am also a named co-inventor on the following patent applications:

Patent/Publication Number	Grant/Publication Date	Official Title (English)
US-2006-0183833-A1	08/17/2006	LOW-COLOR STIFF PVB LAMINATES
US-2005-0288429-A1	12/29/2005	A PROCESS FOR CONTROLLING POLYVINYLBUTYRAL PHYSICAL PROPERTIES BY CONTROLLING STEREOCHEMISTRY OF SAME
US-2005-0234185-A1	10/20/2005	POLYVINYLBUTYRAL INTERLAYER SHEET WITH IMPROVED ADHESION TO GLASS AND A PROCESS FOR PREPARING SAME
US-2006-0008648-A1	01/12/2006	POLYVINYLBUTYRAL INTERLAYERS HAVING SUPERIOR ACOUSTICAL PROPERTIES AND METHOD OF PREPARING SAME
US-2008-0157426-A1	07/03/2008	PROCESS AND APPARATUS FOR REDUCING DIE DRIPS AND FOR CONTROLLING SURFACE ROUGHNESS DURING POLYMER EXTRUSION

The claims of the subject application are directed to a process for preparing a low color, polyvinyl butyral sheet for use in the manufacture of glass laminates. Claim 1 is typical of the independent claims and recites as the first two steps:

(I)   admixing polyvinyl alcohol, butyraldehyde, an acid or mixture of acids, water, and sodium dialkyl sulfosuccinate;

(II)   stabilizing the mixture obtained in step (I) by (a) raising the pH of the mixture to at least pH 10, (b) isolating the polyvinyl butyral resin composition by draining the liquid, and (c) washing the polyvinyl butyral resin composition with neutral pH water;

I am aware that the claims of the subject patent application stand rejected under 35 USC 103(a) as obvious over a number of patent documents including Degeilh (US 4,696,971). Degeilh teaches that the described process should be carried out with sodium dialkyl sulfosuccinate and neutralizing to pH of no more than 5.

All of the work described herein was carried out by me or under my supervision.

The data in this Declaration is based upon actual manufacture of PVB and PVB laminates, and focuses on the neutralization step when dioctyl sulfosuccinate (DOSS) is used. It includes my analysis of PVB laminates made from PVB produced by DuPont using sodium dioctyl sulfosuccinate (DOSS) wherein the neutralization is carried out at different pHs.

One laminate sample representing the invention was made using a flake neutralized at a ph of 10.2. A comparative PVB laminate was made using a flake neutralized at a ph of 8.5. Both were made using DOSS and were made on the same equipment using the same parameters (except neutralization was carried out to the pHs described) by the following steps.

As explained below, laminates were not made using flake neutralized at lower pH because of concern over flammability in the dryer. In addition, the PVB made at pH 4.5 was observed to have higher color than PVB neutralized at higher pHs.

Below is a table listing the ingredients used:

Additive	Comparative Example 1 – pH = 4.5 *Parts (by weight)*	Comparative Example 2 – pH raised to 8.5 *Parts (by weight)*	Invention Example – pH raised to 10.2 *Parts (by weight)*
DuPont™ Elvanol® 71-30 Polyvinyl Alcohol*	72	72	72
DuPont™ Elvanol® 9050 Polyvinyl Alcohol*	28	28	28
High-Purity Butyraldehyde (Eastman Chemicals)	Sufficient amount to achieve a hydroxyl goal of 18.8 wt%#	Sufficient amount to achieve a hydroxyl goal of 18.8 wt%#	Sufficient amount to achieve a hydroxyl goal of 18.8 wt%#
Water	567	567	567
DOSS	0.3	0.3	0.3
Para-Toluene Sulfonic Acid	1.157	1.157	1.157
H_2SO_4	0.402	0.402	0.402
H_3PO_4	0.231	0.231	0.231
Versene™ Ethylene Diamine Tetra-Acetic Acid Sodium Salt (Dow)	0.045	0.045	0.045
1st NaOH Neutralization Step	0.569	0.569	0.569
2nd NaOH Neutralization Step	-	0.310	0.330

*   Contains small amounts of sodium acetate. Product brochures and MSDS enclosed.

\#   The process was conducted the same for each sample during the initial steps prior to neutralization.

The first step of the process used to make the PVB was admixing polyvinyl alcohol, butyraldehyde, an acid or mixture of acids, water, and sodium dioctyl sulfosuccinate at 90°C. The next step involved stabilizing the mixture obtained in the first step by raising the pH of the mixture to 10.2 (invention examples) or 8.5 (comparative example). This was done in two

stages. First the material was taken to a pH of 4.5 to avoid a chemical reaction reversal. During this step the excess butyraldehyde was sparged out to reduce the formation of 2-ethy-2-hexenal. Next the reaction batch of the invention was taken to a pH of 10.2 to avoid excess formation of the fine PVB "gel" which we see in the laminates.   The pH was taken to 8.5 for the comparative example. The invention and comparative sample materials were then further processed by isolating the polyvinyl butyral resin composition by draining the liquid, and washing the polyvinyl butyral resin composition with neutral pH water. That was followed by drying the PVB resin and extruding the PVB resin (flake) with plasticizer and additives at a temperature of from about 209°C to about 210°C to obtain PVB sheeting. The flake neutralized at the two different pH levels was extruded into sheeting using the process described in US 3,153,009 Example (III). From this sheeting standard glass laminates were prepared and examined for clarity.

Here it is noted that while the pH was first taken to a pH of 4.5 it was not feasible to make laminates from that material. That material was determined to be thermally unstable and pose a processing risk of fire in the dryer. Hence, for safety reasons a comparative laminate sample was not prepared from the material that was at 4.5 pH.

I note that in my observations of the three materials, the material that was neutralized at 4.5 pH was the most highly colored and, thus, in addition to its thermal instability, it is my opinion based upon my experience in the art that this material was less suitable for making laminates of the two materials. In addition, it is my opinion (as is confirmed with the data) that the materials neutralized at pH 10.2 had better color than and was better suited for making laminates than the material neutralized at pH 8.5.

After the laminates were prepared I observed both of them. The invention sample laminate was very clear. The comparative sample laminate showed defects. These differences were magnified when viewed under high intensity light, which is common windshield test used in the industry to observe clarity.

I also evaluated the samples under a microscope using UV light and counting and sizing device. Attached is a graph showing the gel counts. The lighter line (blue) to the left, when present, represents the invention and the darker line (red) (to the right) represents the comparative sample. The graph shows that the comparative sample had larger amount and larger size gel particles than the sample representing the invention. Higher quantities of and larger sized gel particles are unacceptable because they are easier to see and scatter light. Thus, the invention provided significantly superior results over the comparative sample.

It is noted that since the material prepared at pH 4.5 had more color than other two samples when observed by eye, it is my opinion that had there been no safety concern and had a laminate been prepared, that sample would have had more gel particles than both the samples prepared at pH 8.5 and pH 10.2.

Given the above, it is my opinion that the invention, which involves use of sodium dialkyl sulfosuccinate (e.g., DOSS) and neutralizing to pH or at least 10, provides better clarity laminates than laminates prepared from PVB sheet made using a process involving sodium dialkyl sulfosuccinate and a neutralization step at lower pHs. The comparative sample neutralized at a ph of 8.5 had more gel counts and was not as clear, and based upon my knowledge in the pertinent art and the results obtained with that sample, as well as based upon my observations of the material prepared at pH 4.5 was not safe to process through the dryer, my expectation is that even worse results would have been obtained had the pH been lower. It is also my opinion based upon my knowledge in this art and based upon the work carried out, that the better clarity obtained with the claimed invention would not be expected based upon the Degeilh and the other documents cited in the rejections.

Based upon my experience in the pertinent art and the work carried out, it is my opinion that the results support that unexpected results are obtained with the invention as claimed and, thus, are commensurate in scope with the claims. Thus, it is my opinion that the invention provides unexpected results over the process described in Degeilh and that these results are significantly better than would be obtained with the process of Degeilh.

All statements made herein of my own knowledge are true, all statements made herein based on information and belief are believed to be true, and further that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001, and may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,
/Donald L. Rymer/

Dated: May 7, 2009

Attachment - Gel Counts of PVB Laminates

Comparison of gel particulate counts

um
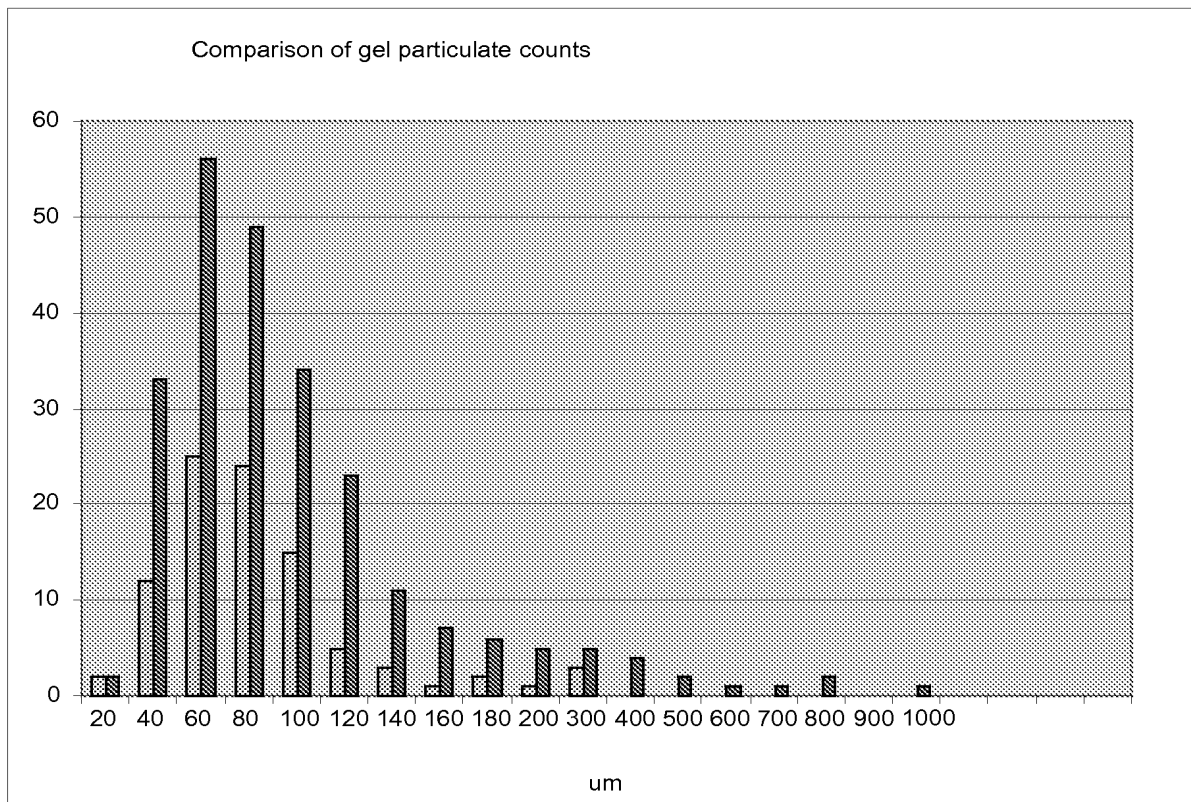
The lighter line (blue) to the left, when present, represents the invention.

The darker line (red) (to the right) represents the comparative sample.

Vinyl Acetal Polymers

Standard Article

Jerome W. Knapczyk[1]

[1]Monsanto Company

VINYL ACETAL POLYMERS

Vinyl acetal polymers are made by the acid-catalyzed acetalization of poly(vinyl alcohol) [9002-89-5] with aldehydes (1).
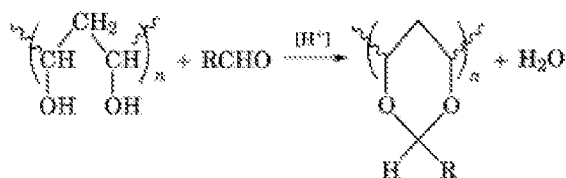
Analogously, poly(vinyl ketals) can be prepared from ketones, but since poly(vinyl ketals) are not commercially important, they are not discussed here. The acetalization reaction strongly favors formation of the 1,3-dioxane ring, which is a characteristic feature of this class of resins. The first of this family, poly(vinyl benzal), was prepared in 1924 by the reaction of poly(vinyl alcohol) with benzaldehyde in concentrated hydrochloric acid (2). Although many members of this class of resins have been made since then, only poly(vinyl formal) [9003-33-2] (PVF) and poly(vinyl butyral) [63148-65-2] (PVB) continue to be made in significant commercial quantities.

Commercialization of PVF and PVB began during the 1930s and 1940s following development efforts by a number of companies, including Union Carbide, DuPont, Shawinigan Chemicals (now Monsanto Chemical), Wacker-Chemie, and I.G. Farben Industrie (now BASF) (3–12). One incentive for this activity was the discovery that safety windshields made with plasticized PVB interlayer offered significant advantages over windshields made with plasticized cellulose acetate, which was then in general use (13, 14).

PVB accounts for about 90% of the poly(vinyl acetal) resin made in the 1990s. Most PVB is plasticized and made into interlayer for vehicle and architectural safety glass, and the remainder is used as an ingredient in a variety of coating, binding, printing, and adhesive applications. PVF accounts for the remaining 10% of the poly(vinyl acetal) made. PVF's primary use is for wire and cable insulation. In this application, PVF is combined with other reactive resins and cured to form tough, chemical- and abrasion-resistant coatings (see Insulation, electric). Applications for PVF and PVB resins make use of the toughness, resilience, optical clarity, high pigment/filler binding capacity, and high adhesion the resins can provide when appropriately formulated.

The poly(vinyl acetal) prepared from acetaldehyde was developed in the early 1940s by Shawinigan Chemicals, Ltd., of Canada and sold under the trade name Alvar. Early uses included injection-molded articles, coatings for paper and textiles, and replacement for shellac. Production peaked in the early 1950s and then decreased as a result of competition from less expensive resins such as poly(vinyl chloride) (see Vinyl polymers, poly(vinyl chloride)). Alvar is no longer manufactured.

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1. Synthesis and Structure

Poly(vinyl alcohol) used to manufacture the poly(vinyl acetal)s is made from poly(vinyl acetate) homopolymer (see Vinyl polymers, vinyl alcohol polymers; Vinyl polymers, vinyl acetate polymers). Hydrolysis of poly(vinyl acetate) homopolymer produces a polyol with predominantly 1,3-glycol units. The polyol also contains up to 2 wt % 1,2-glycol units that come from head-to-head bonding during the polymerization of vinyl acetate monomer. Poly(vinyl acetate) hydrolysis is seldom complete, and for some applications, not desired. For example, commercial PVF resins may contain up to 13 wt % unhydrolyzed poly(vinyl acetate). Residual vinyl acetate units on the polymer help improve resin solubility and processibility (15). On the other hand, the poly(vinyl alcohol) preferred for commercial PVB resins has less than 3 wt % residual poly(vinyl acetate) units on the polymer chain.

Poly(vinyl acetals) are made from poly(vinyl alcohol) and aldehydes by acid-catalyzed addition–dehydration. The mechanism of acetalization has been proposed (16, 17). The degree of acetalization and the conditions used during the reaction significantly affect product properties. Batch and continuous processes in both aqueous and organic media are used during manufacturing. In single-stage batch processes, hydrolysis of poly(vinyl acetate) and acetalization of the poly(vinyl alcohol) hydrolysis product are carried out in the same kettle at the same time. In two-stage batch processes, hydrolysis and acetalization take place in separate kettles.

Assuming that acetalization is irreversible and that both 1,3- and 1,2-glycol units are present in poly(vinyl alcohol), the highest degree of acetalization that can be expected on a statistical basis is 81.6% (18). However, acetalization is reversible (19), and even higher degrees of acetalization are possible (7, 20, 21). For most applications, complete acetalization is not needed, and would be difficult to achieve on a commercial scale without a significant amount of intermolecular acetalization.

Commercial poly(vinyl acetal)s are terpolymers with varying amounts of vinyl acetate and vinyl alcohol units remaining on the backbone after acetalization. The class can be represented by the following structure, showing acetal (**1**), vinyl alcohol (**2**), and vinyl acetate (**3**) units.
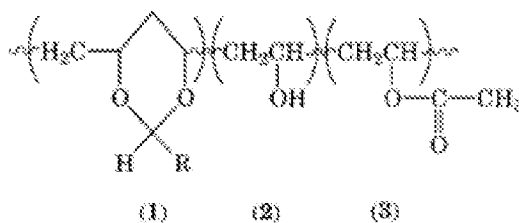
The physical properties of the resin can be modified over a wide range of values because resin properties are a function of the relative amounts of the three monomeric units, average molecular weight, molecular weight distribution, aldehyde chain length, and the stereochemistry of the backbone pendent groups, all of which can be manipulated during manufacturing. Aldehyde blends have also been used to achieve unique properties (22).

Both intramolecular and intermolecular acetalization can occur, although intramolecular acetalization predominates during early stages of the reaction. Late in the reaction intermolecular acetalization begins to take place when isolated hydroxyl groups from two different polymer chains form acetal linkages. As the level of intermolecular acetalization increases, the resin becomes more difficult to process and gel particles form as cross-linked networks begin to build.
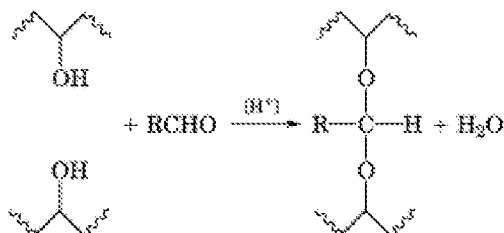
For commercial applications, a small degree of intermolecular acetalization is tolerated and, to a limited extent, it can be manipulated to control the molecular weight distribution of the resin. This in turn affects the solubility and rheological properties of the resin. Other than the possibility of cross-linking, hydrolysis and acetalization do not significantly alter the resin's chain length. Thus the molecular weight of an acetylated resin is largely determined by that of the poly(vinyl acetate) from which it is derived.

The poly(vinyl alcohol) made for commercial acetalization processes is atactic and a mixture of *cis*- and *trans*-1,3-dioxane stereoisomers is formed during acetalization. The precise cis/trans ratio depends strongly on process kinetics (16, 17) and small quantities of other system components (23). During formylation of poly(vinyl alcohol), for example, *cis*-acetalization is more rapid than *trans*-acetalization (24). In addition, the rate of hydrolysis of the *trans*-acetal is faster than for the *cis*-acetal (25). Because hydrolysis competes with acetalization during acetal synthesis, a high cis/trans ratio is favored. The stereochemistry of PVF and PVB resins has been studied by proton and carbon nmr spectroscopy (26–29).

The resin's unacetalated hydroxyl groups take part in both intramolecular and intermolecular hydrogen bonding. Intermolecular hydrogen bonding helps bind individual polymer molecules together, making it more difficult for polymer chains to untangle and slip by each other. Resin glass-transition temperature (T_g), viscosity, modulus, and tensile strength increase as the hydroxyl level increases. Simultaneously, processibility and resiliency are reduced. Backbone hydroxyl groups also can form hydrogen and covalent bonds to the surface of polar substrates and are largely responsible for the adhesion characteristics of this resin class (30).

2. Physical Properties

The thermal glass-transition temperatures of poly(vinyl acetal)s can be determined by dynamic mechanical analysis, differential scanning calorimetry, and nmr techniques (31). The thermal glass-transition temperature of poly(vinyl acetal) resins prepared from aliphatic aldehydes can be estimated from empirical relationships such as equation 1 where OH and OAc are the weight percent of vinyl alcohol and vinyl acetate units and C is the number of carbons in the chain derived from the aldehyde. The symbols with subscripts are the corresponding values for a standard (s) resin with known parameters (32). The formula accurately predicts that resin T_g increases as vinyl alcohol content increases, and decreases as vinyl acetate content and aldehyde carbon chain length increases.

$$T_g = T_g s + 1.26\,(OH - O\,H_s) - 0.6\,(OAc - OAc_s) + 46\ln\,(C_s/C) \qquad (1)$$

Unformulated poly(vinyl acetal) resins form hard, unpliable materials which are difficult to process without using solvents or plasticizers. The solubility parameter ranges for some commercially available PVF and PVB resins are listed in Table 1. Plasticizers not only aid resin processing but also lower the glass-transition temperature, T_g, and can profoundly change other physical properties of the resins. For example, the mechanical glass-transition temperature of a poly(vinyl acetal) plasticized with dibutyl phthalate is reduced by 1.3°C per part of plasticizer added to 100 parts resin (34). Acetalization with longer chain aldehydes (35) and aldehydes

Table 1. Solubility Parameter Ranges for Some Commercial PVF and PVB Resins[a]

Resin	Low hydrogen bonding solvents	Medium hydrogen bonding solvents	High hydrogen bonding solvents
PVF			
low acetate	9.3–10.0	9.7–10.4	9.9–11.8
PVB			
hydroxyl (9–13%)	9.0–9.8	8.4–12.9	9.7–12.9
hydroxyl (17–21%)	[b]	9.9–12.9	9.7–14.3

[a]Ref. 33.
[b]Insoluble.

with polyalkylene oxide chains (36) provides a degree of internal plasticization. Long-chain acetal ends tend to reduce T_g without relying exclusively on liquid plasticizers (37).

Poly(vinyl acetal)s can be formulated with other thermoplastic resins and with a variety of multifunctional cross-linkers. Examples of resins that are at least partially compatible with PVF or PVB resins include some types of polyurethanes (38), polyvinylpyrrolidinone (39), cellulose triacetate (40), nitrocelluloses, poly(vinyl chloride) (41, 42), epoxies, isocyanates, phenolics, silicones, and urea–formaldehyde resins. During the curing step with cross-linkers, which is usually carried out at elevated temperatures, covalent bonds are formed between hydroxyl groups on the poly(vinyl acetal) backbone and the reactive centers on the cross-linker. When cross-linking takes place the resin becomes thermoset. Thermosetting generally increases thermal stability, rigidity, and abrasion resistance, and improves resistance to solvents and to acids and bases. It also severely limits processibility by making the resin insoluble and impossible to extrude.

Although they lack commercial importance, many other poly(vinyl acetal)s have been synthesized. These include acetals made from vinyl acetate copolymerized with ethylene (43–46), propylene (47), isobutylene (47), acrylonitrile (48), acrolein (49), acrylates (50, 47), allyl ether (51), divinyl ether (52), maleates (53, 54), vinyl chloride (55), diallyl phthalate (56), and starch (graft copolymer) (47).

Resins with ionomeric pendent groups have also been prepared by acetalating with an aldehyde containing ionic functionality (57–60). At moderate temperatures the ionic groups cluster to form crystalline-like domains which make the resin stiffer than conventional PVB resins (61). At higher processing temperatures, the crystalline-like domains melt out, resulting in sharper drops in resin viscosity. This reduces stickiness and increases resistance to blocking at ambient temperatures, and lowers melt viscosity and improves flow during higher temperature extrusion and laminating steps compared to conventional PVB resins (62).

3. Health and Safety Factors

Representative unformulated PVB and PVF resins are practically nontoxic orally (rats) and no more than slightly toxic after skin application (rabbits). No mortalities were produced in rats exposed by single inhalation for four hours and no allergic skin reactions were observed in controlled skin contact studies with human volunteers. More specifically, a representative PVB resin is practically nontoxic by single-dose oral ingestion ($LD_{50} > 10.0$ g/kg) or by single dermal applications ($LD_{50} > 7.9$ g/kg), and it is only slightly irritating to the eyes (2.8 on a scale of 0–110) and nonirritating (0 on a scale of 0–8) to the skin of rabbits tested in standard FHSA tests for irritation (63). Unformulated, the resins appear to have no acute toxicological properties that would require special handling other than good hygienic practices. The highest purity grades of PVB can be formulated to meet the extractibility requirements of the FDA, and some can be used in accordance with CFR regulations as ingredients for can enamels, adhesives, and components for paper and paperboard in contact with aqueous and fatty foods (33).

Table 2. Physical Properties of Butvar Resins

Property	Method	B-72	B-74	B-76	B-90	B-98
molecular mass × 10^3 (avg)	a	170–250	120–250	90–120	70–100	40–70
viscosity 15 wt %, $Pa·s$[b]	c	7–14	3–7	0.5–1	0.6–1.2	0.2–0.4
viscosity 10 wt %, $Pa·s$[b]	d	1.6–2.5	0.8–1.3	0.2–0.45	0.2–0.4	0.07–0.2
Ostwald soln viscosity, $mPa·s$[b] (=cP)	e	170–260	40–50	18–28	13–17	6–9
specific gravity, 23°C/23°C	ASTM D792-50	1.100	1.100	1.083	1.100	1.100
refractive index	ASTM D542-50	1.490	1.490	1.485	1.490	1.490
vinyl alcohol content, wt %		17–20	17–20	11–13	18–20	18–20
vinyl acetate content, wt %		0–2.5	0–2.5	0–1.5	0–1.5	0–2.5

[a]Determined by size exclusion chromatography in tetrahydrofuran with low angle light scattering.
[b]To convert $Pa·s$ to P, multiply by 10.
[c]Measured in 60:40 toluene:ethanol at 25°C using a Brookfield viscometer.
[d]Measured in 95% ethanol at 25°C using an Ostwald-Cannon-Fenske viscometer.
[e]B-72 in 7.5 wt % anhydrous methanol at 20°C; B-76 and B-79 in 5.0 wt % SD 29 ethanol at 25°C; B-74, B-90, and B-98 in 6.0 wt % anhydrous methanol at 20°C, all using an Ostwald-Cannon-Fenske viscometer.

OSHA and ACGIH have not established specific airborne exposure limits for PVB and PVF resins; however, some products may contain sufficient fines to be considered nuisance dust and present dust explosion potential if sufficient quantities are dispersed in air. Unformulated PVB and PVF resins have flash points above 370°C. The lower explosive limit (lel) for PVB dust in air is about 20 g/m².

Many grades of PVB and PVF resins are made, and most are eventually compounded and used as multicomponent products. Individual product MSDSs need to be consulted prior to handling and each product should be handled appropriately and in accordance with good industrial hygiene and safety practices, which include appropriate skin, respiratory, and eye protection.

4. Poly(vinyl butyral)

Monsanto, DuPont, Hoechst, Sekisui, and Wacker Chemie are major manufacturers of PVB resins. Several grades are available that differ primarily in residual vinyl alcohol content and molecular weight. Both variables strongly affect solution viscosity, melt flow characteristics, and other physical properties. The physical, mechanical, and thermal properties of various grades of Monsanto's Butvar resins are listed in Tables 2, 3, 4, respectively. In general, resin melt and solution viscosity increase with increasing molecular weight and vinyl alcohol content, whereas the tensile strength of materials made from PVB increases with vinyl alcohol content for a given molecular weight.

Commercially available PVB resins are generally soluble in lower molecular weight alcohols, glycol ethers, and certain mixtures of polar and nonpolar solvents. A representative list is found in Table 5. Grades with lower vinyl alcohol content are soluble in a wider variety of solvents. A common solvent for all of the Butvar resins is a combination of 60 parts of toluene and 40 parts of ethanol (95%) by weight. pt

PVB resins are also compatible with a limited number of plasticizers and resins. Plasticizers (qv) improve processibility, lower T_g, and increase flexibility and resiliency over a broad temperature range. Useful plasticizers include dibutyl and butyl benzyl phthalates, tricresyl and 2-ethylhexyl diphenyl phosphates, butyl ricinoleate, dibutyl sebacate, dihexyl adipate, triethylene glycol di-2-ethylbutyrate, tetraethylene glycol diheptanoate, castor oil, and others (64–73).

PVB combinations with the thermoplastic resins nitrocellulose or shellac have been used as sealers for wood finishing. In these applications the PVB component adds flexibility and adhesion. Tough, optically

Table 3. Mechanical Properties of Butvar Resins

Property	ASTM method	B-72	B-74	B-76	B-90	B-98
tensile strength, MPa[a]						
yield	D638-58T	47–54	47–54	40–47	43–50	43–50
break		48–55	48–55	32–39	39–46	39–46
elongation, %						
yield	D638-58T	8	8	8	8	8
break		70	75	110	110	110
modulus of elasticity, GPa[b]		2.28–2.34	2.28–2.34	1.93–2.0	2.07–2.14	2.14–2.21
flexural strength yield, MPa[a]	D790-59T	83–90	83–90	72–79	76–83	76–83
hardness, Rockwell						
M	D785-57	115	115	100	115	110
E		20	20	5	20	20
impact strength, J/m[c]	D256-56[d]	58.7	58.7	42.7	48	37.4

[a]To convert MPa to psi, multiply by 145.
[b]To convert GPa to psi, multiply by 145,000.
[c]To convert J/m to ft·lb/in., divide by 53.38.
[d]Notched Izod (1.27×1.27 cm (0.5×0.5 in.)).

Table 4. Thermal Properties of Butvar Resins

Property	Method	B-72	B-74	B-76	B-90	B-98
flow temperature, °C, 6.9 MPa[a]	ASTM D569-59	145–155	135–145	110–115	125–130	105–110
T_g, °C	[b]	72–78	72–78	62–72	72–78	72–78
heat distortion temperature, °C	ASTM D648-56	56–60	56–60	50–54	52–56	45–55
heat sealing temperature, °C	[c]	220	220	200	205	200

[a]6.9 MPa = 1000 psi.
[b]By differential scanning calorimetry from 30 to 100°C on dried resin.
[c]Dried film (0.025 mm) on paper cast from 10 wt % resin in 60:40 toluene:ethanol; heat sealer dwell time, 1.5 s at 0.4 MPa (60 psi).

clear blends have been made with aliphatic polyurethanes (74). Conducting polyacetylene exhibits enhanced stability under ambient conditions when blended with PVB (75). Thermosets are prepared with cross-linkers that form covalent bonds with hydroxyl groups. Cross-linking resins include select isocyanate, phenolic, and epoxy resins. Lower molecular weight organic cross-linkers include dialdehydes, isocyanates, and etherified melamines. Inorganics that can function as cross-linkers include chromic, boric, and phosphoric acid and their derivatives (76).

4.1. Manufacture

PVBs are manufactured by a variety of two-stage heterogeneous processes. In one of these an alcohol solution of poly(vinyl acetate) and an acid catalyst are heated to 60–80°C with strong agitation. As the poly(vinyl alcohol) forms, it precipitates from solution (77). Ethyl acetate, the principle by-product, is stripped off and sold. The precipitated poly(vinyl alcohol) is washed to remove by-products and excess acid. The poly(vinyl alcohol) is then suspended in a mixture of ethyl alcohol, butyraldehyde, and mineral acid at temperatures above 70°C. As the reaction approaches completion the reactants go into solution. When the reaction is complete, the catalyst is neutralized and the PVB is precipitated from solution with water, washed, centrifuged, and dried. Resin from this process has very low residual vinyl acetate and very low levels of gel from intermolecular acetalization.

Table 5. Solubility of Butvar Resins[a]

Solvent	B-72; B-74[b]	B-76; B-79[c]	B-90; B-98[c]
acetic acid (glacial)	S	S	S
acetone	I	S	SW
butyl acetate	I	S	PS
N-butyl alcohol	S	S	S
butyl cellosolve	S	S	S
cyclohexanone	S	S	S
diacetone alcohol	PS	S	S
diisobutyl ketone	I	SW	I
N,N-dimethylacetamide	S	S	S
N,N-dimethylformamide	S	S	S
dimethylsulfoxide	S	S	S
ethyl acetate (99%)	I	S	PS
ethyl alcohol (95%; anhydrous)	S	S	S
ethylene dichloride	SW	S	SW
ethylene glycol	I	I	I
isophorone	PS	S	S
isopropyl alcohol (95%; anhydrous)	S	S	S
isopropyl acetate	I	S	I
methyl acetate	I	S	PS
methyl alcohol	S	SW	S
methyl ethyl ketone	SW	S	PS
methylene chloride	PS	S	S
methyl isobutyl ketone	I	S	I
naphtha (light)	I	SW	I
N-methyl-2-pyrrolidinone	S	S	S
propylene dichloride	SW	S	SW
tetrachloroethylene	SW	SW	SW
tetrahydrofuran	S	S	S
toluene	I	PS	SW
toluene:ethanol, 95% (60:40 by wt)	S	S	S
1,1,1-trichloroethane	SW	S	SW
xylene	I	PS	SW

[a]S, soluble; PS, partially soluble; I, insoluble; and SW, swells.
[b]Employed 5% solids mixture agitated for 24 h at ambient temperature.
[c]Employed 10% solids mixture agitated for 24 h at ambient temperature.

In the second stage of a representative aqueous process, an aqueous solution of poly(vinyl alcohol) is heated with butyraldehyde [123-72-8] and an acid catalyst (78, 79). PVB precipitates from solution as it forms. After 2–3 h at a temperature of about 90°C, when the reaction is complete, the acid is neutralized and the resin is washed, filtered, and dried. While the cost of solvent handling is minimal in this process, it is offset somewhat by the need for separate hydrolysis and acetalization facilities. Because PVB resin precipitates early in the reaction there is a tendency toward high levels of intermolecular acetalization. Cross-linking can be minimized by adding emulsifiers to control particle size (80–84) or substances like ammonium thiocyanate (85), or urea (86) to improve the solubility of PVB in the aqueous phase. To increase the average molecular weight of the resin small quantities of a dialdehyde like glutaraldehyde can be added during the acetalization step (87).

4.2. Applications

During 1994, about 68,000 t of unplasticized PVB was manufactured worldwide. Of this, the overwhelming majority, about 66,000 t, was plasticized and extruded into sheet for use in laminated safety glass. Only about 2,300 t of unplasticized PVB was used for noninterlayer applications.

4.2.1. Laminated Glass

About 1.5×10^8 m^2 of safety glazing interlayer was manufactured worldwide in 1994. About 75% of this was used for vehicle windshields and most of the rest was used for laminated architectural glazing (88, 89) and a variety of security glass applications (90). Major producers of interlayer for laminated glass are Monsanto (Saflex), the largest producer, followed by DuPont (Butacite), Sekisui (S'Lec) and Hüls (Trosofoil).

Plasticized PVB is uniquely suited for safety and security glazing applications. It is easily extruded into sheet. The laminated sheet exhibits high adhesion to glass, optical clarity, stability to sunlight, and high tear strength and impact-absorbing characteristics, all of which are demanded for safety glazing use. In windshields, for example, the interlayer serves several potentially life-saving functions. It adheres to glass shards after a glass-breaking impact, thereby helping to reduce injury from flying glass. After the glass is broken during an impact, the interlayer's high tear strength and resiliency acts like a safety net by absorbing enough energy to resist penetration by a projectile or a vehicle occupant's head (91). In addition to its safety features, laminated glass in architectural applications adds sound attenuation, heat insulation, and break-in security, and also blocks uv radiation.

Most laminated safety glazings are glass–PVB–glass trilayer composites, but bullet- and projectile-resistant laminates. Laminates for other specialty uses may be made with more than three layers. In addition to glass, poly(ethylene terephthalate) (PET), acrylic, and polycarbonate structural components (92) are used in specialty laminated glazing products.

Many grades of interlayer are produced to meet specific length, width, adhesion, stiffness, surface roughness, color (93, 94), and other requirements of the laminator and end use. Sheet can be supplied with vinyl alcohol content from 15 to about 23 wt %, depending on the supplier and application. A common interlayer thickness for automobile windshields is 0.76 mm, but interlayer used for architectural or aircraft glazing applications, for example, may be much thinner or thicker. There are also special grades to bond rear-view mirrors to windshields (95, 96) and to adhere the components of solar cells (97, 98). Multilayer coextruded sheet, each component of which provides a separate property not possible in monolithic sheet, can also be made (99–101).

Adhesion of plasticized PVB to clean glass is very high. It is postulated that both hydrogen bonds and silyl alkyl ether covalent bonds are formed between resin hydroxyl groups and silanol groups at the interlayer–glass interface (30) (Fig. 1). However, the surface chemistry of float glass is complex, and both moisture and low concentrations of ionic substances at the interlayer–glass interface affect adhesion. Thus, interlayer–glass adhesive strength depends not only on the interlayer's formulation and moisture content, but also on the type, age, and condition of the surface of the glass. Salts and moisture are thought to reduce adhesion by competing with resin hydroxyls for bonding sites on the glass surface.

Because there is an inverse relationship between interlayer–glass adhesive strength and laminate penetration resistance, adhesion must be carefully controlled in safety glass applications. If adhesion is too low, glass retention during an impact will be sacrificed even though the interlayer is not penetrated. If adhesion is too high, a projectile can easily penetrate the laminate because cracks made in the glass propagate through the interlayer. In order for the interlayer to cushion an impact, enough debonding must take place in the laminate to allow the interlayer to expand after the glass is cracked.

One measure of impact resistance is the laminate's mean break height (MBH) (102). In the standard test, there is a 50% probability that a five-pound (2.27-kg) ball will not fall through a laminate if the ball is dropped at the MBH. Typical MBHs for 12 in. (~ 30 cm) square laminates prepared with 30 mil (0.76 mm) thick
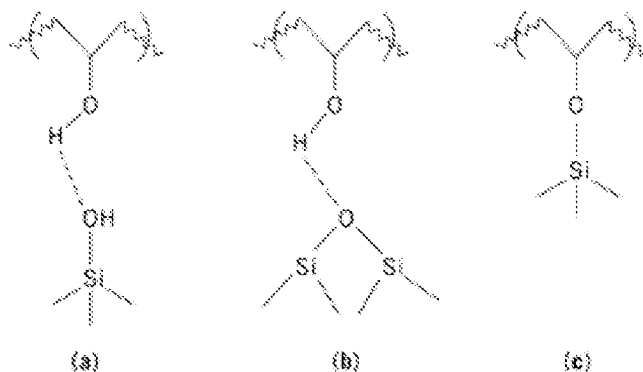
Fig. 1. Hydrogen and covalent bonds can form between the resin's hydroxyl groups and the surface of glass: (**a**) a hydrogen bond to a silanol group; (**b**) a hydrogen bond to a silyl ether oxygen; and (**c**) an ether-type covalent bond.
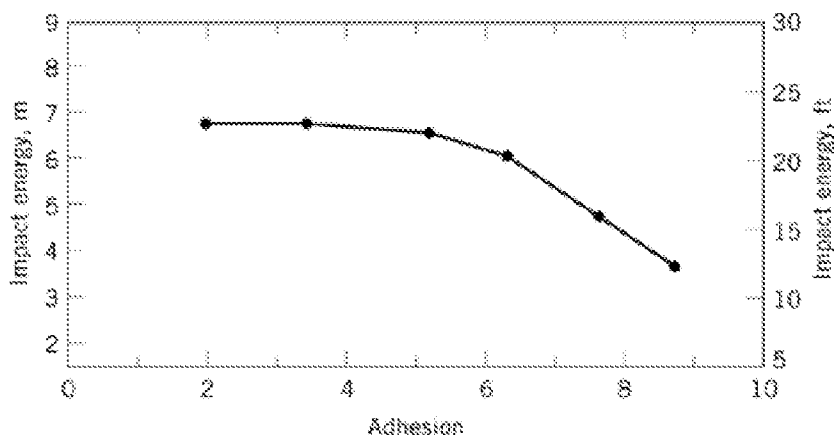
Fig. 2. Typical impact energy vs adhesion (10 is high, 0 is no adhesion) curve obtained from the mean break height test carried out at 21°C with a 2.27 kg ball on 30-cm square laminates. Mean break height dramatically declines when adhesion is at high levels.

interlayer are 10 ft ($\sim$3 m) at 0°F (-18°C) and 15 ft ($\sim$4.6 m) at 70°F (21°C). Figure 2 shows a relationship between adhesion and falling ball penetration resistance measured at 21°C.

To maximize penetration resistance without danger of delamination during impact or aging, adhesion to glass is reduced from inherently high levels (10, in Fig. 2) to intermediate levels ((3–7), in Fig. 2) by adding parts per million quantities of Group Ia or IIa alkanoate salts (103–113) or surfactants (114) to the resin. It is not clear how these additives influence adhesion, but they also strongly affect the product's moisture sensitivity and some other performance attributes. Often adhesion fine tuning is carried out on the interlayer after it is extruded by adjusting the interlayer moisture level to between 0.2 and 1%.

Plasticized PVB interlayer is hygroscopic. In addition, T_gs are in the neighborhood of 30°C; thus, interlayer tends to adhere to itself, or block, when rolls or stacks of cut blanks are stored at ambient conditions. For these reasons handling and shipping must be carried out under controlled humidity and at temperatures well below the sheet's T_g. Precut interlayer blanks and rolls are usually stored or shipped refrigerated (3–10°C), and when rolls need to be stored or shipped at ambient conditions, the sheet is interleaved with a thin sheet of nonadhering plastic such as polyethylene.

To help prevent air from being trapped between glass and interlayer surfaces during lamination, the interlayer surface is textured during manufacture (115–120). The textured surface provides pathways for air to escape. Several methods are used to de-air during lamination. In one, the sheet is positioned between two pieces of glass and the prelaminate is tacked together by nipping the sheet between large rubber rolls at about 38°C. The sandwich is then heated to about 50–75°C and subjected to an additional nipping step to eliminate most of the remaining air and seal the edges. Excess sheet at the edges is trimmed with a trimming tool. Finally, the laminate is autoclaved at 135–150°C for 30–120 min in pressurized air, 1.3–1.8 MPa (13 to 18 kg/cm²), or in sealed bags under vacuum (121). During lamination, full adhesion and optical clarity are attained as the softened interlayer flows and wets the glass. Any remaining trapped air dissolves into the sheet.

Interlayer with various widths of gradient color bands are made for automobile windshields (122–124). The band is added by printing the interlayer surface or by coextruding previously mixed dyed or pigmented resin. Before laminating, gradient interlayer is often shaped to accommodate the curvature of the windshield. This is accomplished by differentially stretching sheet heated at about 85–100°C over a tapered shaping drum. The hot sheet is then cooled with cold air, cut into blanks, and stacked prior to laminating.

4.2.2. Noninterlayer Applications

Some categories of nonglazing uses for PVB are as follows:

Phenolic/adhesives	Coatings/additives
adhesives/sealants/gaskets	wash primers
abrasives and break pad binders	wood coatings
printed circuit boards	paint and varnish additives
structural composites/laminates	maintenance, metal, and
	industrial coatings
Metal/glass binders	wire enamels
metal oxide binders	can coatings
retroreflective coatings	foil coatings
glass optical coatings	nail polish
Hard copy printing	Others
inks	pest strips
toners	powder coatings
photoimaging	miscellaneous
reprographics	

For most of these, the resin serves as a film-forming additive, an adhesive, and/or as a binder for pigments, fillers, metal oxides, ceramics, and other materials. The resin provides toughness and flexibility and adheres strongly to additive particles and to glass or other polar surfaces. For example, PVB binds the glass beads used in retroreflective films for licence plates, decals, and road signs. It also helps bind the retroreflective films to the surfaces of which they are applied. PVB is used to bind metal oxide particles during the fabrication of certain glasses, ceramics (125–127), and superconductors (128). PVB resin is also used to make membranes for fuel cells (129), gas–liquid separators (130), and ultrafiltration devices (131).

PVB is used as a film-forming component in corrosion-inhibiting primers for metals called wash primers or metal conditioners. The primers have good adhesion to ferrous metal surfaces and form a good foundation for various types of topcoats. The primers act by stabilizing the metal oxide surface and by continuously supplying corrosion-inhibiting ions such as chromate (132). Formulations containing nontoxic corrosion-inhibiting ions have also been made (133, 134). Wash primers are used on storage tanks, bridges, ships, highway guard rails, and on submerged structures (76, 135).

Aqueous dispersions of plasticized PVB are used for many coating applications (136, 137). The dispersions are manufactured by intensive kneading of the resin in the presence of a plasticizer, surfactant, and water (138–140). Generally, the dispersions are about 50% solids, including about 40 parts of plasticizer per 100 parts of resin. Cast, air-dried films are tough and transparent and adhere to many materials. They are resistant to water and grease, which makes them useful as coatings for grease-proof washable wallpaper, window shades, and packaging materials. Properly formulated, they can be used for strippable or temporary protective coatings.

PVB dispersions are widely used in the textile industry to impart abrasion resistance, durability, and fiber strength. They have been used for finishing nylon webbing for parachute harnesses and seat belts. They can be applied to textiles by spraying, from a dilute bath by impregnation on a padder, or from a thickened dispersion by coating on spreading equipment. The dried dispersion imparts a soft, full-bodied finish to rayon, cotton, or nylon and helps prevent raveling of filament yarns. PVB dispersions have been used to finish curtain and drapery fabrics and upholstery goods, to join fabric to fabric and other materials, and as a component in transparent rug backings.

5. Poly(vinyl formal)

Estimated worldwide production of poly(vinyl formal) resin was about 2700 t in 1994. PVF resins are currently manufactured by Wacker Chemie (Pioloform F) in Germany and by Chisso (Vinylec) in Japan. Chisso purchased Monsanto's PVF (Formvar) business in 1992. The Vinylec resins are free-flowing white powders with a poly(vinyl formal) content of about 81 wt %. The properties of representative grades are listed in Table 6. Chemical resistance of Vinylec to acids, bases, and aliphatic hydrocarbons is excellent, and chemical resistance to alcohols, aromatic hydrocarbons, esters, and ketones is good; however, chemical resistance to chlorinated solvents is rated poor (141). Residual vinyl acetate and vinyl alcohol component levels are 9–13 wt % and about 5 wt %, respectively. Grades are available with average molecular weights from about 25,000 to 100,000.

Table 6. Properties of Vinylec Poly(vinyl formal) Resins[a]

Property	Value
specific gravity	1.1–1.3
tensile strength, MPa[b]	49–78
flexural strength, MPa[b]	108–127
hardness, Shore	70–80
flow temperature, °C	140–150
heat distortion temperature, °C	84–93
dielectric strength, kV/mm	26–39
dielectric constant, 60 Hz	3.0–3.7
volume resistivity, $\Omega \cdot cm$	10^{14}–10^{16}
dissipation factor, 60 Hz	0.006–0.015

[a]Ref. 141.
[b]To convert MPa to psi, multiply by 145.

In general, PVF resins are soluble in a limited number of solvents and in certain mixtures of alcohols and aromatic hydrocarbons.

The solubility of representative poly(vinyl formal) resins is as follows in single solvents, where S = soluble and I = insoluble:

acetic acid (glacial)	S	chloroform	S
monochloro acetic acid	S	ethylene dichloride	S
benzyl alcohol	S	acetone	I
dioxane	S	carbon disulfide	I
cresol	S	ethyl alcohol	I
tetrahydrofuran	S	ethyl acetate	I
dimethyl sulfoxide	S	butyl acetate	I
methyl benzoate	S	methyl ethyl ketone	I
N,N-dimethylformamide	S	cyclohexanone	I
N,N-dimethylacetamide	S	nitropropane	I
xylenol	S	hydrocarbons	
furfural	S	aliphatic	I
pyridine	S	aromatic	I

For mixed solvents, PVF is soluble in toluene:ethyl alcohol (95%) (60:40 wt %) and xylene:methyl alcohol (60:40 wt %), but insoluble in toluene:butyl alcohol (60:40 wt %) and xylene:butyl alcohol (60:40 wt %). The solubility of PVF resins in polar solvents increases with increasing proportions of residual vinyl acetate content. Increasing vinyl acetate content also reduces resin stiffness and tensile and impact strength. Solution viscosity increases with increasing vinyl alcohol content and with the average molecular weight of the resin. Although moderate increases in the average molecular weight of the various commercial grades do not substantially affect tensile strength, modulus, and some other physical properties of the unmodified resins, they strongly increase solution viscosity.

PVF resins are generally compatible with phthalate, phosphate, adipate, and dibenzoate plasticizers, and with phenolic, melamine–formaldehyde, urea–formaldehyde, unsaturated polyester, epoxy, polyurethane, and cellulose acetate butylate resins. They are incompatible with polyamide, ethyl cellulose, and poly(vinyl chloride) resins (141).

Commercial PVF is manufactured by a single-stage batch process in acetic acid (142–144). In the single-stage process, hydrolysis and formalization take place concurrently. In one process, poly(vinyl acetate) is dissolved in an aqueous mixture of acetic acid and formaldehyde. Sulfuric acid catalyst is added and the mixture is maintained at 75–85°C for about 6–8 h or until the reactions are completed. The average molecular weight of the product is largely determined by the average molecular weight of the poly(vinyl acetate) charge. The ratio of vinyl acetate and vinyl alcohol components in the acetal product is controlled by the ratio of acetic acid, water, and formaldehyde used. When the reaction is complete, the mineral acid is neutralized. As water is added to the agitated mixture, PVF resin precipitates as fine, off-white granules. Color can be improved by adding antioxidants during formalization (145). The resin is centrifuged and dried after washing with water to remove salt and organic by-products. In this process, hydrolysis of poly(vinyl acetate) is the rate-controlling step.

5.1. Applications

PVF resins are used almost exclusively to make electric and magnetic wire insulation. In these applications the PVF resin component helps provide toughness, as well as abrasion and thermal resistance. The resin is combined with phenolic, epoxy, melamine, or other resins capable of cross-linking with hydroxyl groups in suitable vehicles to produce formulations called wire enamels (146–149). A typical wire enamel consists of 100 parts of PVF and 50 parts of a cresol–formaldehyde resin dissolved in a mixture of cresylic acid and

naphtha solvent (150). The enamels are coated on copper or aluminum wire and cured in ovens at elevated temperatures to form thermoset coatings with good thermal stability, insulating properties, and abrasion and chemical resistance (151). Magnetic wire insulation made with PVF wire enamels performs well on high speed motor winding equipment and maintains good insulating properties at the elevated temperatures generated during motor overloads.

PVF resins have also been used in a variety of other applications, including conductive films (152), electrophotographic binders (153), as a component for inks (154), and in membranes (155, 156), photoimaging (157), solder masks (158), and reprographic toners (159).

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JEROME W. KNAPCZYK
Monsanto Company

Related Articles

Insulation, electric; Vinyl acetate polymers

Laminated Materials, Glass

Standard Article

R. Terrell Nichols[1] and Robert M. Sowers[2]

[1]Ford Motor Company
[2]Consultant, Ford Motor Company

LAMINATED MATERIALS, GLASS

A laminate is an orderly layering and bonding of relatively thin materials. A commonly laminated material is glass. Most commonly, two pieces of float or sheet glass are bonded with poly(vinyl butyral) [9003-62-7] (PVB) (see Vinyl polymers, poly(vinyl acetals)) to produce a highly transparent safety glass, eg, an automotive windshield. This combining of transparent abrasion-resistant glass and resilient plastic achieves the durability and safety demanded of such products. Other materials that may be incorporated in laminated glass are colorants, electrically conducting films or wires, and rigid plastics. The value of the laminate is the utilization of the desirable properties from each of the constituents. In the case of laminated glass, the excellent weathering properties of the glass protect the impact energy-absorbing plastic interlayer from deterioration, abrasion, and soiling.

Benedictus, a French chemist who accidentally broke a flask that contained dried-on cellulose nitrates, is credited with founding the laminated-glass industry (1). The first patent was issued in 1906 (2). The growth of the laminated glass market was slow until automobile numbers and automotive speeds increased to the point that glass-caused injury was of concern. By the late 1920s, laminated windshields were standard in automobiles. The most common construction was two pieces of plate glass bonded with cellulose nitrate. However, the plastic interlayer introduced problems of haze, discoloration, and loss of strength, and it was replaced by cellulose acetate in 1933. Cellulose acetate demonstrated improved stability to sunlight but lacked strength over a broad temperature range and produced haze. The advent of the poly(vinyl butyral) resins in 1933 permitted the development of the modern interlayers that are used to make the majority of laminated safety glass in use; the resins were adopted for all automotive laminates by 1939.

Laminated glass is not a true composite material. The glass needs the safety net effect of the interlayer if impacted, and the interlayer needs the durability and rigidity of the glass for useful service other than during impacts. Exceptions where laminated glass more truly fits the definition of a composite are when it is used for noise attenuation (see Insulation, acoustic) or bullet resistance. In these applications, the alternate layering of rigid and soft materials achieves results beyond those produced by either alone.

1. Properties

Laminated materials frequently have limits on properties below those found in one of the components. Laminated glass with a PVB interlayer has a maximum service temperature not exceeding 70°C, far below that of solid glass. The strength of laminated glass is dependent on the number, thickness, and strength of the individual glass plies and on the characteristics of the particular interlayers used. For the majority of laminates consisting of two plies of annealed glass and one PVB interlayer, the bending strength is about 0.6 of that for an equal thickness of solid glass.

Glass–PVB laminates become more rigid with a decrease in temperature, and below −7°C approach the performance of solid glass. At temperatures above 38°C these laminates are less rigid and provide improved penetration resistance. Some applications utilize heat-strengthened or tempered glass for additional strength.
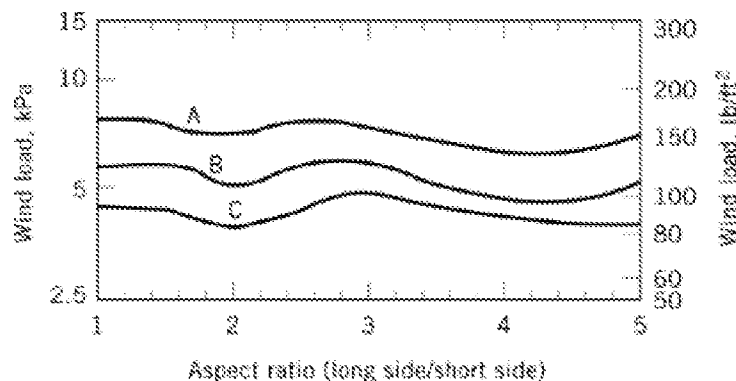
Fig. 1. Wind-load data for heat-strengthened and laminated 3.2-mm glass. Architect's specified probability of breakage is 8/1000 laminates for a 1-min uniform wind-load duration. Four sides supported in weathertight rabbet. Curves for different glazing areas: A, 0.93 m^2 (10 ft^2); B, 1.39 m^2 (15 ft^2); C, 1.86 m^2 (20 ft^2).(Courtesy of PPG Industries, Inc.)
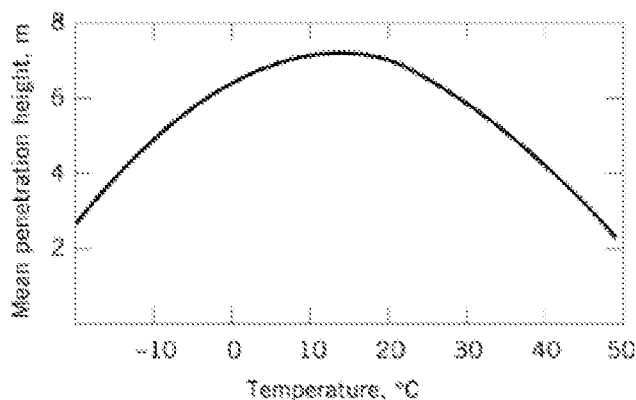

Fig. 2. Typical pen etration resistance vs temperature data from laboratory procedure ($_{305 \times 305-mm}$ laminates, 0.76-mm PVB; 2.27-kg ball impact).(Courtesy of Monsanto Co.)

Figure 1 is an example of a wind-load chart for the combination of heat-strengthened and laminated glass (3). Wind-load information is used jointly by the architect, glazing contractor, and glass manufacturer to determine the permissible glazing area and glass thickness required to meet the design wind load.

Most laminated glass applications are concerned with impact strength, and minimum performance levels are required by specification. The impact strength of two plies of laminated, annealed glass and various PVB thicknesses are available (4). Aircraft laminates may utilize electrical resistance heating as deicing for vision enhancement.

Automotive and architectural laminates of PVB develop maximum impact strength near 20°C, as shown in Figure 2. This balance is obtained by the plasticizer-to-resin ratio and the molecular weight of the resins. It has been adjusted to this optimum temperature based on environmental conditions and automobile population at various ambient temperatures. The frequency and severity of vehicle occupant injuries vs temperature ranges at the accident location have been studied (5), and the results confirm the selection of the maximum performance temperature and decreasing penetration resistance at temperature extremes.

The optical properties of laminated glass are required to be equal to solid glass, because most applications are in vision areas. Light scattering by the interlayer essentially is nonexistent if PVB with the correct index
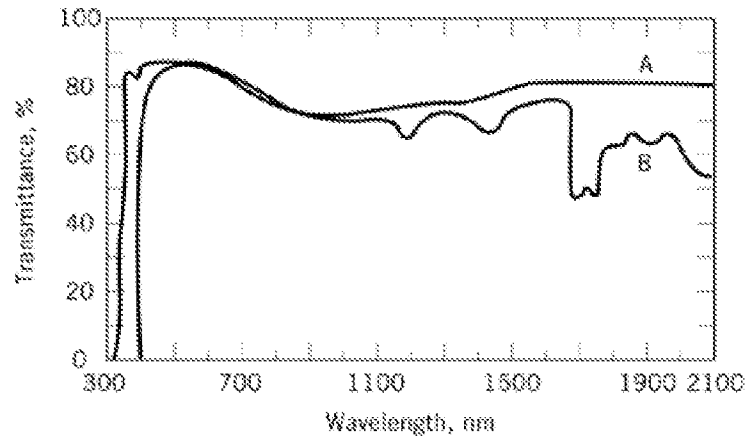
Fig. 3. Visible-light transmittance of automotive laminate: A, 475-mm monolithic glass; B, 5-mm laminated glass.(Courtesy of Ford Motor Co.)

of refraction is used. Clean-room practices can reduce the dust and lint that is attracted to the surfaces (see Sterilization techniques). Visible-light transmittance of a typical automotive laminate (2.1-mm glass, 0.76-mm PVB, 2.1-mm glass) is nearly equal to solid glass of the same thickness (Fig. 3), and noticeable color change usually is absent. Visible-light transmittance is about 88% for clear glass laminates and ranges from 70 to 80% for windshields made with tinted glass. Sunroof laminates have been made with as little as 4% transmittance to reduce solar load. All uv light is absorbed below 370 nm and several discrete absorption bands are in the infrared beyond 1100 nm. The uv absorption may be enhanced when additional protection of color dyes is required, eg, gradient shade bands in automotive windshields or merchandise in window displays. Generally, the solar uv transmittance is on the order of 30–35%, and the infrared is about 97% for 0.76-m thick PVB.

The index of refraction of PVB (1.48) is close enough to glass (1.520) to couple the two glass plies with a reflectance loss of only 0.02%:

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \qquad (1)$$

where R is the reflectance at the interface and n_1 and n_2 are the different refractive indexes. The absorption coefficient for visible light (400–700 nm) generally is -0.25 to -0.45 for PVB. This produces a transmission loss within the PVB of 0.7–1.3%, which is mostly in the blue and ultraviolet portion of the spectrum.

Subsequent to the lamination process, some defects may appear that were not visible previously in the glass. One of these phenomena is called a bull's eye when found in windshields. These are small depressions that are formed in the glass pair during bending by the presence of glass chips or other debris between the plies. Upon lamination, the pockets fill with PVB and become convex lenses. Conversely, shallow ridges on an internal glass surface may be absorbed in the PVB and the optics are improved. Various other optical distortions may be caused by nonparallel plies of glass or PVB.

2. Manufacture

Practically all conventional laminated glass utilizes plasticized poly(vinyl butyral) (PVB) as the interlayer. Curved, laminated windshields are by far the principal products; silicone and cast-in-place urethane resins are sometimes used in specialty applications. Laminators purchase PVB in rolls up to 500-m long, up to

270-cm wide, and from 0.38- to 1.52-mm thick. There are several placticizers used and at different ratios of plasticizer-to-resin content, depending on the product being manufactured. Flexol 3 GH, (bis(2-ethylbutanoic acid), triethylene glycol ester), manufactured by Union Carbide, is utilized at about 44 parts per 100 parts of resin. Other plasticizers (qv) used are di-n-hexyl adipate and dibutyl sebacate. There are at least five companies offering these products with manufacturing facilities in the United States, Japan, Belgium, Germany, and Mexico. Because the plastic is an adhesive material, it is shipped either with a dusting or parting agent on the surface or is refrigerated so it does not cohere. The refrigerated material is clean, moisture adjusted, and ready to laminate. The dusted material requires washing and moisture conditioning. Removal of the parting agent by warm water, followed by a chilled water rinse, adds about 0.2% water content to the plastic which must be compensated either by overdrying before washing, or drying after washing so as to achieve the desired 0.3–0.5% H_2O content. These steps are done more efficiently on the continuous roll before cutting. Moisture content of the PVB is extremely important because it has a direct effect on the adhesion characteristics of the glass/plastic surfaces.

The drying stage is carefully controlled to relax the sheeting of physical stresses as well as to adjust the moisture content. It consists of draping the sheeting over slat conveyors or driven rolls in a temperature- and humidity-controlled oven. The gradient band sunshade that appears in many windshields is either printed continuously on the interlayer roll at the PVB manufacturing plant or extruded into the sheet at the time of manufacture. To permit a more pleasing conformance to the curved glass, the banded interlayer may be preshaped which causes the extremities of the band to be more nearly parallel the horizon in the installed windshield. The shaping of the interlayer may be carried out on the continuous roll using a cone-shaped expander prior to cutting the blanks (6). The radius of curvature is preset, depending on the pattern of the particular windshield being manufactured. The interlayer then is cut to approximate laminate size and accumulated in low stacks (150 mm max) ready for assembly. Another method for shaping the interlayer involves warping in special ovens after the blanks are cut. The interlayer stacks must be stored in cooled, moisture-controlled rooms to control water absorption and blocking of the highly plasticized material.

The glass for laminating may be annealed, heat-strengthened, tempered, flat or curved, clear or colored. Thicknesses of $\geq 1.5 - 12$ mm are used. For flat laminates, the glass is cut to size, edged and treated, if specified, washed, and delivered to the clean room by conveyor. The washing process, in addition to cleaning, can affect the interlayer bond. Common water hardness residues at invisible levels can reduce adhesive strength of PVB to glass. The desired level is achieved by controlling the hardness of the final rinse water and by removing the water by air stripping as opposed to evaporative drying. The glass is cooled during drying to prevent premature sticking when the interlayer is placed on the glass, thereby permitting easier positioning of the components.

In order to manufacture curved laminates, the glass is preshaped before laminating. This is usually accomplished by simultaneously bending a pair of glass templates which are cut to the shape of the finished windshield and separated by an inert powder to prevent fusing of the plies. The bending process is typically carried out on a peripheral support, metal fixture, or mold; the pair slowly travels through a lehr so that the glass sags to shape by the force of gravity. Glass temperatures of 600°C are required to achieve the shape, and the shaping is followed by annealing to reduce stress. Banded windshields usually are constructed with one or more pieces of tinted, heat-absorbing glass to enhance occupant comfort and to reduce air-conditioning load.

The clean room typically is operated at 18°C and 26% rh, which produces an equilibrium condition for the desired interlayer moisture level. The interlayer is placed on one piece of glass, with the gradient band, if present, carefully positioned above the designated eye position. The adjacent piece is superimposed, excess interlayer is trimmed, and this "sandwich" is conveyed from the room through a series of heaters and rolls that press the assembly together while expelling air. Temperature is increased stepwise to 90°C and pressures of 170–480 kPa (25–70 psi) are applied. Solid rubber rolls usually are used with flat laminates, and curved glass requires segmented rolls on a swivel frame (Fig. 4) (7, 8). For more complex shapes, peripheral gaskets may be applied and the assembly may have the air evacuated (9), or the entire assembly may be placed in a bag and the air evacuated. The bag may or may not be removed prior to autoclaving, but when using an oil autoclave
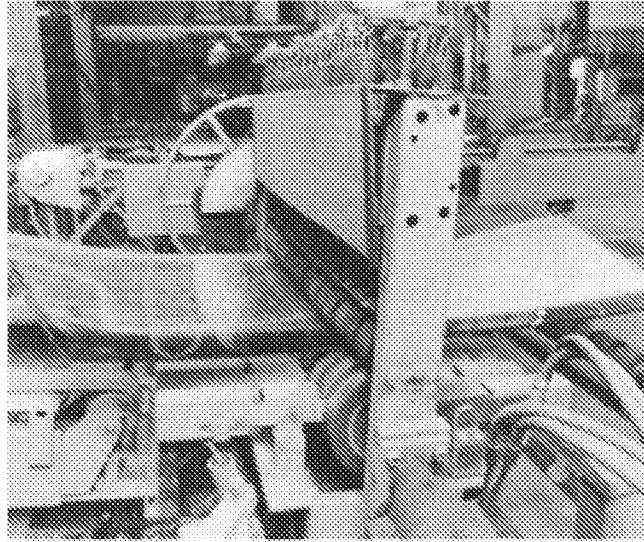
Fig. 4. The glass and vinyl "sandwich" is fed through a special de-air machine to remove trapped air and increase the adhesion of the vinyl to the glass.(Courtesy of Ford Motor Co.)

where the oil would damage one of the components, an oil-resistant Teflon or poly(vinyl alcohol) bag can be used (10). The tacked assembly is loaded onto racks for autoclaving, which may be either in an air or oil vessel capable of pressing the sandwiches at 1.38–1.72 MPa (200–250 psi) and 100–135°C for 30–45 min. Curved laminates and multiple laminates may require longer cycles to allow the polymer material to flow completely.

In the autoclave cycle, the pressure is increased more rapidly than the temperature and then is maintained toward the end of the cycle as the temperature is lowered, to prohibit bubble formation and reduce any chance of delamination. The exit temperature must be no greater than 50°C to avoid thermal breakage. During the cycle, residual air is absorbed by the interlayer, and the embossed surface of the interlayer flows and wets the glass surface, thereby producing the clear laminate. Occasional small residual bubbles of trapped air can be removed by an additional autoclaving cycle. The air autoclave process is becoming the preferred method because it eliminates the subsequent washing of oily residues that are produced in oil autoclaving. The elimination of the process oil and subsequent washwater waste products also are environmental improvements. In some cases, additional trimming of the interlayer or finishing of the glass edge is required. The protruding interlayer may be trimmed or removed by wire brushing, but care must be taken to assure that the glass edge is not damaged in the process. The labeling of safety glass is done by grit-blasting through a mask or by silk-screening of a ceramic frit enamel. A final step in some windshield manufacture is the bonding of a small metal plate to the windshield. This plate, which is used to support the rearview mirror, is laminated to the glass using a special formulation of poly(vinyl butyral).

Radio antennas have been incorporated in some windshield models by inclusion of a very fine copper wire placed across the top of the windshield and vertically at the center. The wire is tacked to the interlayer prior to assembly and is embedded into the interlayer during autoclaving. An electrical connector that is soldered to the antenna wire is bonded to the bottom edge of the windshield for ease of connection. This type of construction is, however, being increasingly replaced by silk-screening of the antenna patterns directly on the glass using a silver-frit mixture.

3. Production and Shipment

Chemical attack, particularly from moisture and alkaline conditions, is prevented by use of acidic packing materials and open, ventilated packages. Good crate design and proper handling throughout shipment avoids mechanical damage. Glass-to-glass contact is never permitted. Long-term storage must be in well-ventilated areas, never in sealed containers. In the case of trans-ocean shipping, however, sealed containers are often used with a desiccant added to prevent moisture attack of the glass (see Desiccants).

Flat laminates are separated only by newsprint or plastic beads (ie, Lucite) and are bound into a block to prevent movement between the laminates. Curved laminates are spaced to prevent abrasion and require supporting dunnage at several points to prevent breakage by excessive flexing during shipment. Banding and blocking are designed to add compressive forces only. Staining is not a problem in the uncovered areas, but the supporting members are specified to have an acidic content to prevent chemical attack.

Laminated glass products are considered noncombustible and are shipped without DOT hazardous warning labels. Flat laminate packs, because of their high density, do not fill the car or trailer and require sturdy bracing to prevent shifting. Glass products are shipped and stored in a vertical plane, and during transportation they are placed so that each plate has an edge in the direction of travel.

4. Economic Aspects

The growth of laminated glass closely followed the growth of motor vehicles from the late 1920s to the 1960s. Windshields and side glasses of all domestic vehicles were laminated during this period. In the early 1960s, the flat, laminated, side glass was almost entirely replaced by curved, tempered glass. The curved windshield laminated glass market continued to follow automotive trends, but the flat glass products redeveloped around architectural uses. Architectural products currently represent 5–10% of the laminated glass volume. Increased consumer safety awareness and security needs are expanding the flat laminate market. Safety codes (eg, 16CFR 1201 and ANSI Z97.1) specify laminated glass as one means of meeting their requirements (11, 12). In hurricane-prone areas laminated glass is being specified increasingly by local authorities.

Laminated windshields, as opposed to tempered glass windshields, are gaining in market share outside of North America. From 37% of the non-North American market of 1976, they were estimated to have reached 75% by 1982 (13). In addition to North America, Belgium, Italy, and the Scandinavian countries permit only laminated windshields, and other nations are increasing use by customer option. The trend toward laminated windshields is expected to continue and nonlaminated windshields will likely be obsolete by the year 2000 (14).

5. Specifications

Almost all of the laminated glass made is tested and certified to comply with certain safety performance standards. In the United States, there are two types of standards: automotive and architectural. For the former, *ANSI Z26.1-1973* is used and is incorporated in the Federal Motor Vehicle Safety Standard 205 (15). It specifies safety performance, durability, and optical quality. Specific tests are required depending on the location in the vehicle where the glazing is to be used. Item 1, the most difficult to meet, may be used in any location in the vehicle. It requires, in addition to other tests, support of a 2.3-kg ball dropped from 3.7 m onto a 305-mm square of laminate. Item 2 (safety glazing for any location except windshields) may be met by laminated glass using thinner PVB because it does not require the 2.3-kg ball test and the optical distortion tests. Laminated glass may also be used in locations specifying item 3 (no visible transmittance requirement) or item 11A (bullet-resistance glass; also requires appropriate tests, eg, ballistic tests). Automotive safety glass

is required to be labeled as to the manufacturer, code, item, and model number that identifies the type of construction.

Conformance to the standard is achieved by submitting samples to an approved laboratory for evaluation and submitting the laboratory report to the American Automotive Manufacturers Association (AAMA). The approved certificate is sent to the manufacturers with copies to the state and provincial jurisdictions for which the AAMA serves as approvals agent (16).

Laminated glazing materials used in building locations specified by federal regulations are certified to comply to federal standards by the Safety Glazing Certification Council (SGCC) (17). Other locations requiring safety glazing specified by state or local code may use alternative standards (12). Glass complying to these standards is labeled permanently as to the standard (or standards) that it meets, including thickness, identification of the manufacturer, and plant. Also, it usually contains a date of manufacture. In situations where the large laminated sheets are cut into smaller pieces by the local distributor or installer, each piece is permanently labeled to indicate that it was cut from glass meeting the standard.

Certification to these standards is obtained by submitting a test report from an approved laboratory to the SGCC. Once certified, the product is assigned an SGCC certification number to identify it and the factory at which it was made. Subsequently, samples are selected randomly by the administrator at least twice a year to ensure continued adherence to the standard. Based on these re-evaluation reports, SGCC authorizes continued use of the certification label and the product listing published in its directory. The building standards are concerned mainly with body impact, and they require testing by impact on the glazing with a 45-kg bag. Detailed testing procedures and interpretations are available (11, 12).

Bullet-resistant glass products are tested according to UL 752 (18). The test specifies that three shots are fired from 4.6 m and impacting within 100 mm of each other in a triangle, and that there is no penetration of the projectile nor any glass embedded in the corrugated board. The level of approval is determined by the velocity and energy level of the bullet at the muzzle of the firearm. Additional tests required include impacts 38 mm apart and tests over temperature ranges of 13–35°C for indoor use and -31.7 to 49°C for outdoor use.

The above-mentioned codes contain requirements for accelerated durability tests. In addition, interlayer manufacturers and laminators expose test samples for several years under extreme weather conditions, eg, the Florida coast and Arizona desert. The laminated products weather extremely well, with no change in the plastic interlayer. Occasionally, clouding is noted around the edges when exposed to high humidity for long periods, but this is reversible. Colored areas of PVB laminates may fade while subjected to extensive uv/solar irradiation, which could cause an appearance issue. This has not, however, been shown to alter the laminate's other performance properties.

6. Analytical and Test Methods

Interlayer moisture is one of the important controls for PVB-to-glass adhesion of current formulations (although moisture-insensitive formulations are being developed). The moisture content equilibrates with the relative humidity to which the interlayer is exposed and thus is variable. Prior to lamination, interlayer moisture content is measured by one of three methods. The most rapid is by air absorption using a spectrophotometric technique to determine a ratio of the 1925-nm to the 1705-nm wavelength peak (Fig. 3). A slower but less expensive method is weighing the interlayer before and after vacuum desiccation. The third and classical method is by Karl Fisher reagent; this technique is usually confined to instrument calibration exercises. The infrared method, in addition to being the most rapid, permits measurement of the interlayer moisture content while the interlayer is in the laminate. Instrumentation is available for monitoring interlayer moisture in full-size parts.

Interlayer bond strength is determined by either pummeling the laminate at -18°C to break away the glass and to determine the amount of adhering glass particles or by compressively shearing the laminate
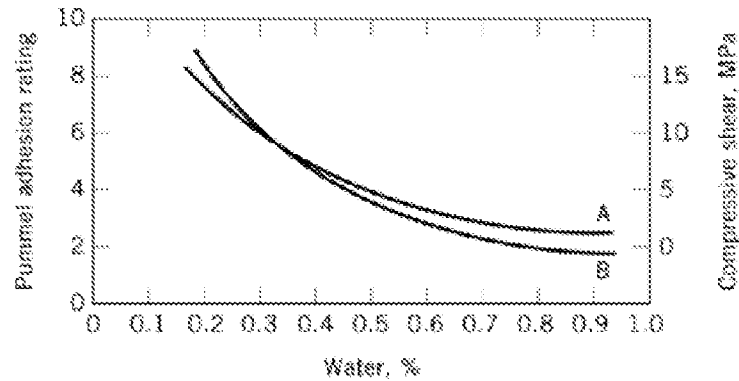
Fig. 5.   Typical effect of moisture on PVB adhesion: A, pummel data $_{(-20°C)}$ from Monsanto Co.; B, compressive shear data from Du Pont Co. To convert MPa to psi, multiply by 145.
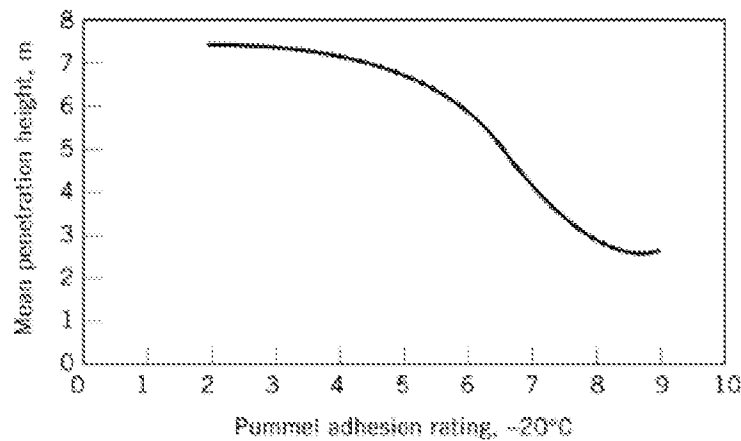
Fig. 6.   Typical variation of mean penetration height with adhesion (2.27-kg ball, impact at $_{-2°C}$ on $_{305×305-mm}$ laminates; 0.40%water, 0.76-mm PVB).(Courtesy of Monsanto Co.)

sample in a universal test machine. The optimum pummel range is three to five units on an arbitrary scale (from 1 to 10) established by the industry. The relationship of pummel value and compressive shear data to water content of the interlayer is given in Figure 5 and that of pummel value to mean penetration height is given in Figure 6. These data are influenced also by residual hardness of the water used to wash the glass.

Subsequent to processing, an inspection is made for incomplete bonding, inside dirt, and glass quality. In the case of windshields, rigid optical standards must be met, and these must be evaluated for the completed windshield. Extensive test requirements are described in the appropriate codes (11, 12, 15, 18–24), and they include light stability, resistance to optical distortion, humidity, boil test, abrasion resistance, and assorted impact tests.

7. Uses

7.1. Penetration-Resistant Windshields

Performance difference between windshields manufactured in Germany and the United States was reported in the early 1960s (25, 26). Three variables contribute to the greater safety of the German windshields against impact: thinner glass (especially the inboard member), thicker plastic interlayer, and higher moisture content of the interlayer. The latter acts as a plasticizer and in adhesion control (see Plasticizers). By reducing the adhesion of the interlayer to the glass, more interlayer area can be released and stretched during impact. Also, the thicker interlayer, in addition to having more inherent strength, causes more fracturing of the glass during impact than in the older model of windshield. This, in turn, increases the amount of released interlayer for impact energy absorption. Upon review by the SAE Glazing Committee, it was agreed that the improvement was desirable, if it could be accomplished without taking the risk of increased water content. The U.S. PVB manufacturers subsequently developed controlled adhesion interlayers without increasing moisture above the previous standard content, and the glass fabricators utilized this material to produce laminated windshields with more than twice the impact resistance of the pre-1966 windshields. This product was introduced in limited production in 1965 and was used in all United States car lines for the 1966 models (27).

The ASA (now ANSI) performance code for Safety Glazing Materials was revised in 1966 to incorporate these improvements in windshield construction. The addition of test no. 26 requiring support of a 2.3-kg ball dropped from 3.7 m defined this level of improvement. It was based on a correlation established between 10-kg, instrumented, head-form impacts on windshields, on $0.6 \times 0.9-m$ flat laminates, and the standard $0.3 \times 0.3-m$ laminate with the 2.3-kg ball (28). Crash cases involving the two windshield interlayer types were matched for car impact speeds and were compared (29). The improved design produced fewer, less extensive, and less severe facial lacerations than those produced in the pre-1966 models.

Additional improvements have been incorporated since 1966 with the availability of thinner float glass. Glass thickness and interlayer thickness have been studied to optimize the product for occupant retention, occupant injury, and damage to the windshield from external sources (30, 31). The thinner float glass windshields are more resistant to stone impacts than the early plate glass windshields. The majority of laminated windshields are made of two pieces of 2–2.5 mm annealed glass and 0.76 mm of controlled adhesion interlayer.

7.2. Special Laminated Windshields

Combinations of strengthened glass and interlayer offer advantages of lessened weight, higher impact resistance, lowered laceration potential, and resistance to bending stresses. These may be needed in high speed aircraft, helicopters, and motor vehicles. The additional strengthening can be achieved by chemical or thermal processes. The chemical process by ion exchange in molten potassium salts produces highly compressed skin and increases center tension. Thermal processes, capable of inducing high stress into float glass are also widely used, although not usually in automotive windshields.

Another variation of special construction (bilaminate) windshields consists of one ply of glass and one ply of an abrasion-resistant plastic. Although these laminate types have been available for several years, their limited mechanical durability has resulted in limited acceptance. Other features, such as deicing/defogging and solar rejection, can be incorporated into laminated glass. As technology advances it is anticipated that variable light transmission will also be possible by utilizing the properties of liquid crystal or electrochromic materials. These likely will need to be protected from the environment by encapsulation in laminated glass.

Other automotive uses of laminated glass include colored glass and decorated glass. The privacy glass used in the side and rear glazing of vans can be made by laminating one or more layers of highly tinted PVB and clear glass. Opera windows containing metallic ornaments and sufficient plastic interlayer to accommodate
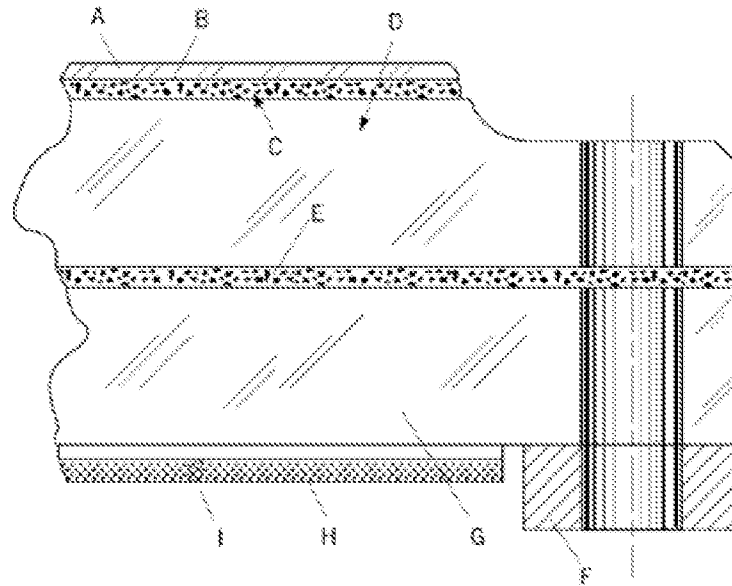
Fig. 7. Cross section of Sierracin windshield used on Boeing 747 (32): A, 2.2-mm chemically strengthened glass; B, Sierracote 3 conductive coating; C, 1.9-mm PVB; D, 23-mm stretched acrylic; E, 1.3-mm PVB; F, laminated cloth spacer ring; G, 23-mm stretched acrylic; H, 0.6-mm PVB; and I, 3.0-mm Sierracin 900.

their thickness have also been used. Laminated roof glazing can consist of a combination of coated glass and a colored PVB.

7.3. Aircraft Windshields

Aircraft windshields have extreme requirements in service temperature and pressurization and they must be resilient against high velocity bird impact. In addition, they must offer excellent visibility, both from optics and deicing capabilities, and an aerodynamic design. These highly specialized windshields are produced in low volume and are made by few companies, eg, Sierracin, PPG Industries, and Triplex Safety Glass Co. Construction varies with the need and service potential of the aircraft. Small planes of limited altitude and speed usually have acrylic monolithic windshields treated with a hardcoat material such as polysiloxane. Slower commercial aircraft use flat laminated glass made with aircraft-grade PVB (Monsanto Saflex PT). These aircraft require deicing capability which may be given by a conductive film that is pyrolytically or vacuum deposited on a glass surface, or conductive plastic film that is laminated in the sandwich. The third general class of aircraft windshield is for the modern, commercial, wide-body aircraft. These windshields become extremely complex, large in size, and expensive. A fourth type is for high speed, low flying military aircraft where birds, high skin temperature, and gunfire warrant extremely complex construction. The third and fourth types are multilayer constructions; typical examples are shown in Figures 7 and 8 (32, 33).

The Boeing 747 windshield (Fig. 7) is about 1.0×1.1 m and is curved to increase the pilot viewing area and to reduce air drag and air noise. Composed of seven plies, it weighs about 64 kg (32). The outer strengthened glass skin and the inner plastic shield may be replaced when damaged. The Triplex Safety Glass Co. also makes wide-body aircraft windshields, flat and curved, for Boeing and others. For the Boeing 747, two precurved, 12-mm plies of Ten-Twenty glass are laminated with PVB and covered with a 3-mm ply of Ten-Twenty glass bent
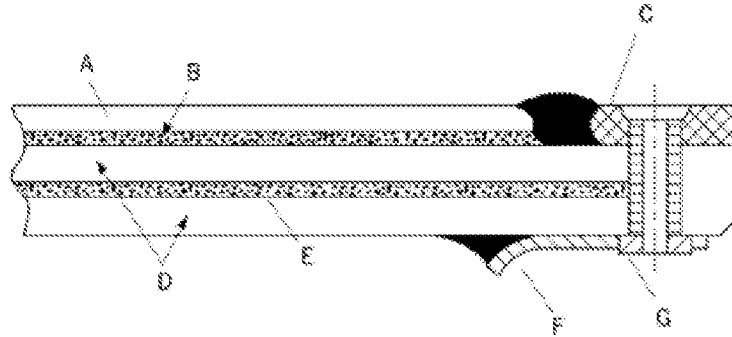
Fig. 8. Sierracin lightweight, birdproof F-111 windshield cross section (43). A, 3.0-mm as-cast acrylic face ply; B, S-100 silicone interlayer; C, fiber glass retainer; D, 6.4-mm polycarbonate structural ply; E, S-120 polyurethane interlayer; F, stainless steel bearing strip; and G, stainless steel bushing.

to conform to the curved windshield. An electrically conductive coating, Hyviz, is applied to the inner surface of the outer ply and then is laminated to the 12-mm Ten-Twenty ply (34).

The construction of the F-111 windshield shown in Figure 8 replaced a glass–silicone laminate previously used. The all-plastic windshield has improved impact resistance so that it is birdproof to 250 m/s (33). In this instance, the scratch resistance of glass was waived to obtain the impact performance at the allowed weight.

7.4. Architectural Products

Many specialized laminated glasses are made for architectural needs such as safety, sound attenuation, solar control, and security. These products may be further enhanced with colors and patterns for decorative effects. Safety glasses are specified in potentially higher risk breakage areas and overhead or sloped glazing (defined as more than 15° from vertical). Overhead glazing materials have varied in the past but more localities are accepting laminates. Sloped and overhead glazing frequently have heat-strengthened or tempered glass used in the construction of the laminate (35). Vertical passageway glazing usually is a 0.76-mm interlayer and sloped glazing is constructed with a 1.52-mm interlayer to accommodate the waviness of heat-treated glasses when they are used.

Noise attenuation is achieved effectively with laminated glass by the combination of the vibration damping effect of the plastic interlayer, an air gap, and usually an unbalanced glass thickness. Typical construction is 0.76–1.5-mm interlayer laminated with 3–10-mm glass. The type of glass or strength is not a factor in noise attenuation but a dead air space can be particularly effective in reducing selected frequencies. A Sound Transmission Class Index of 34–41 is achieved with single laminate glazing and can be improved if combined with double glazing that has large air spaces. Mounting of the glass in an airtight but flexible gasket reduces sound transmission (36). Airports, hotels, factory offices, and control rooms benefit from laminated acoustical glazing (37) (see Insulation, acoustic.

Laminated glass is used for solar control, particularly where a highly reflective surface is not desired and where the laminate contributes other benefits. In these applications, a uniformly pigmented interlayer is obtained from the manufacturer and the laminate can be prepared by the conventional process. Broad ranges of colors and transmission levels are available with shading coefficients as low as 0.41. Pigmented interlayer is considered to be more color stable than dyed interlayer. Browns, blues, greens, pink, white, and clear plastics containing uv absorbers are readily available. Body-colored glasses may be used also, usually with clear interlayer. In these cases, the laminate is dependent only upon the solar properties of the glass.

Laminated glass may also be made using any of the low emittance (low-e) glass products on the market, but the low-e coating must not be in contact with the interlayer for the low emittance property to be achieved.

All laminated glass increases the level of security to some extent. However, depending on the application, security glass is constructed of multiple layers of glass, PVB, polycarbonate, polyurethane, or other polymer materials. Laminated glass permits the same visual observation as normal glass but prevents or delays unauthorized entry (or exit) until the attempt can be detected. It complies with test UL 972 (38).

Bullet-resistant glass is contructed of many layers of glass and aircraft-type PVB depending on the level of resistance desired. Typical products are 38–50 mm thick and weigh $90 - 130 \text{ kg/m}^2$.

A third type of security glass is installed in modern penal institutions. This product is utilized for prisoner detention and obviates iron bars and their demeaning aspect. Typical construction utilizes three or more layers with at least one ply of thick PVB. Other constructions utilize polycarbonates, polyurethanes, and modified acrylics. Strengthened glass and electrically conductive circuits for alarms may be included. Large, heavy sections of similar construction have been used for underwater windows for boats, submarines, and aquariums. Four plies of fully tempered, 10-mm glass plus three plies of $\sim$1.9−mm PVB totaling 44.5 mm in thickness has a modulus of rupture of 172 MPa (25,000 psi) (39).

Glazing of laminated architectural glass requires additional care in the selection of sealants and drainage design. Sealants (qv) must be free of solvents (particularly aromatics) and mineral or vegetable oils (3) and must not provide pockets that would trap water at the glass–PVB edge. Similarly, the glazing detail must be designed with proper drainage (35). Generally, the practice is similar to that of glazing organically sealed insulating units (40, 41).

In the 1990s increased attention has been placed on the design and evaluation of transparent, architectural glazing panels that offer protection from sustained wind and snow loads, as well as gusts of hurricane strength winds (42, 43). Research at academic institutions has been aimed toward improving window performance during extreme weather conditions. Many of the recommended penetration-resistant construction types consist of glass–plastic laminates (44, 45).

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R. TERRELL NICHOLS
Ford Motor Company
ROBERT M. SOWERS
Consultant, Ford Motor Company

Related Articles

Insulation, acoustic; Vinyl polymers, poly(vinyl acetals); Laminated materials, plastic

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        "ELVANOL" POLYVINYL ALCOHOL ALL IN SYNONYM LIST NOL001B
NOL001B   Revised 31-JAN-2008

CHEMICAL PRODUCT/COMPANY IDENTIFICATION

Material Identification

    "ELVANOL" is a registered trademark of DuPont.

Tradenames and Synonyms

    "ELVANOL" 20-25
    "ELVANOL" 71-30
    "ELVANOL" 71-41
    "ELVANOL" 90-50
    "ELVANOL" 90-50PF

Company Identification

    MANUFACTURER/DISTRIBUTOR
                    DuPont Packaging & Industrial Polymers
                    1007 Market Street
                    Wilmington,DE 19898

    PHONE NUMBERS
       Product Information   : 1-(800)-441-7515
       Transport Emergency   : 1-(800)-424-9300
       Medical Emergency   : 1-(800)-441-3637

    COMPOSITION/INFORMATION ON INGREDIENTS

Components

  Material   CAS Number   %
  VINYL ALCOHOL POLYMERS & COPOLYMERS   9002-89-5   0-99
                                              25213-24-5   0-99
                                              54626-91-4   0-99
 *METHANOL, BULK   67-56-1   <1.4
 *METHANOL, PACKAGED   67-56-1   <1.8
  SODIUM ACETATE   127-09-3   <3
  PROCESS AIDS   0-4

  * Disclosure as a toxic chemical is required under Section 313 of
  Title III of the Superfund Amendments and Reauthorization Act of 1986
  and 40 CFR part 372.

HAZARDS IDENTIFICATION

Potential Health Effects

    ADDITIONAL HEALTH EFFECTS

    Before using "ELVANOL" Polyvinyl Alcohol read DuPont Bulletin,
    "Safe Handling Information".

    ACUTE OR IMMEDIATE EFFECTS: ROUTES OF ENTRY AND SYMPTOMS

    INGESTION Not a probable route of entry. Toxicity is predicted
    to be low.

    SKIN Based on experience with handling these polymers and others
    which are similar chemically, no unusual dermatitis hazard is
    expected from routine handling.

    EYE Mechanical irritation only.

    INHALATION "ELVANOL" is supplied as a granular solid. Under
    certain conditions of use, dust may be formed. Treat this dust as
    a nuisance dust; use a dust mask if dust exceeds the recommended
    limits. "ELVANOL" is rarely heated above 100 degrees C. If the
    temperature exceeds 200 degrees C, fumes irritating to the eyes,
    nose, and throat will be evolved. If exposed to these fumes, the
    eyes will tear, itch, and turn red. The nose will burn. The
    throat will burn and coughing may result.

    CHRONIC EFFECTS None are known.

    MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE None are known.

    METHANOL

    The fatal dose of Methyl Alcohol by ingestion is from 60 to 250 ml.

    Inhalation of Methyl Alcohol may cause irritation of the nose and
    throat with sneezing, sore throat or runny nose.

    Skin contact with Methyl Alcohol may cause irritation with
    itching, burning, redness, swelling or rash. Skin permeation may
    occur in amounts capable of producing the effects of systemic
    toxicity.

    Eye contact with Methyl Alcohol may cause eye irritation with
    tearing, pain or blurred vision.

    Ingestion of Methyl Alcohol may cause irritation of the digestive
    tract with stomach pain, heartburn, nausea, vomiting or diarrhea;
    however there may be no symptoms at all.

(HAZARDS IDENTIFICATION - Continued)

Inhalation, ingestion or skin contact with Methyl Alcohol may
cause temporary mild depression of the central nervous system with
dizziness, confusion, incoordination or drowsiness followed by an
asymptomatic period usually ranging from 12 to 24 hours.
Metabolic acidosis develops followed by ocular toxicity (visual
disturbance including blindness). Other effects include
non-specific effects such as headache, nausea and weakness. Gross
overexposure may cause pathological changes in the liver and
kidneys; nerve damage with numbness, weakness or muscle rigidity;
tremors; convulsions; and fatality.

Increased susceptibility to the effects of Methyl Alcohol may be
observed in persons with pre-existing disease of the nervous
system, visual system, liver, kidneys, and cardiovascular system.

Carcinogenicity Information

None of the components present in this material at concentrations
equal to or greater than 0.1% are listed by IARC, NTP, OSHA or ACGIH
as a carcinogen.

FIRST AID MEASURES

First Aid

   INHALATION

   If exposed to fumes from overheating or combustion, move to fresh
   air. Consult a physician if symptoms persist.

   SKIN CONTACT

   In case of contact, immediately wash skin with soap and water.
   Wash contaminated clothing before reuse.
   If molten material gets on skin, cool rapidly with cold water. Do
   not attempt to remove material from skin. Obtain medical treatment
   for thermal burn.

   EYE CONTACT

   In case of contact, immediately flush eyes with plenty of water
   for at least 15 minutes. Call a physician.

FIRE FIGHTING MEASURES

Flammable Properties

   Flash Ignition Temperature: No Data Available

   Fire and Explosion Hazards:

(FIRE FIGHTING MEASURES - Continued)

    The solid polymer can be combusted only with difficulty. Dust
    from "ELVANOL" can form an explosive mixture in the air.
    Information about special precautions needed for bulk handling is
    available upon request.

    HAZARDOUS COMBUSTION PRODUCTS Complete combustion gives
    carbon dioxide and water. Incomplete combustion gives, in
    addition, carbon monoxide and hydrocarbon oxidation products
    including organic acids, aldehydes and alcohols, oxides of
    sodium.

Extinguishing Media

    Water, CO2, Foam.

Fire Fighting Instructions

    Wear self-contained breathing apparatus (SCBA) and full protective
    equipment.

ACCIDENTAL RELEASE MEASURES

Safeguards (Personnel)

    NOTE: Review FIRE FIGHTING MEASURES and HANDLING (PERSONNEL)
    sections before proceeding with clean-up. Use appropriate
    PERSONAL PROTECTIVE EQUIPMENT during clean-up.

Spill Clean Up

    Sweep up to avoid slipping hazard.

HANDLING AND STORAGE

Handling (Personnel)

    See FIRST AID and PERSONAL PROTECTIVE EQUIPMENT SECTIONS.

Storage

    Store in a cool, dry place. Keep containers tightly closed to
    prevent moisture absorption and contamination.

EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls

    In the event the polymer is heated above 200 C (392 F), local
    ventilation should be used to avoid exposure to fumes. Use
    ventilation to avoid exposure of personnel to dust.

Personal Protective Equipment

    EYE/FACE PROTECTION

    Wear safety glasses. Wear coverall chemical splash goggles and
    face shield when possibility exists for eye and face contact due
    to splashing or spraying of molten material. A full face mask
    respirator provides protection from eye irritation.

    RESPIRATORS

    A NIOSH/MSHA approved air purifying respirator with an organic
    vapor cartridge with a dust/mist filter may be permissible under
    certain circumstances where airborne concentrations are expected
    to exceed exposure limits. Protection provided by air purifying
    respirators is limited. Use a positive pressure air supplied
    respirator if there is any potential for an uncontrolled release,
    exposure levels are not known, or any other circumstances where
    air purifying respirators may not provide adequate protection.

    PROTECTIVE CLOTHING

    If there is potential contact with hot/molten material, wear heat
    resistant clothing and footwear.

Exposure Guidelines

 Applicable Exposure Limits
   VINYL ALCOHOL POLYMERS & COPOLYMERS
   PEL   (OSHA)   : None Established
   TLV   (ACGIH)   : None Established
   AEL * (DuPont)   : 10 mg/m3, 8 & 12 Hr. TWA, total dust
                             5 mg/m3, 8 & 12 Hr. TWA, respirable dust

   METHANOL, BULK
   PEL   (OSHA)   : 200 ppm, 260 mg/m3, 8 Hr. TWA
   TLV   (ACGIH)   : 200 ppm, 8 Hr. TWA, Skin
                             STEL 250 ppm
   AEL * (DuPont)   : 200 ppm, 8 & 12 Hr. TWA, Skin

   METHANOL, PACKAGED
   PEL   (OSHA)   : 200 ppm, 260 mg/m3, 8 Hr. TWA
   TLV   (ACGIH)   : 200 ppm, 8 Hr. TWA, Skin
                             STEL 250 ppm
   AEL * (DuPont)   : 200 ppm, 8 & 12 Hr. TWA, Skin

   SODIUM ACETATE

                   (Applicable Exposure Limits - Continued)

```
    PEL   (OSHA)                 : None Established
    TLV   (ACGIH)                : None Established
    AEL * (DuPont)               : 10 mg/m3, 8 & 12 Hr. TWA, total dust
                                   5 mg/m3, 8 & 12 Hr. TWA, respirable dust
```

    * AEL is DuPont's Acceptable Exposure Limit. Where governmentally
    imposed occupational exposure limits which are lower than the AEL
    are in effect, such limits shall take precedence.

PHYSICAL AND CHEMICAL PROPERTIES

Physical Data

```
    Melting Point              : Approximately 200 deg. C (392 deg. F)
    % Volatiles                : 5 WT%
    Solubility in Water        : Moderate solubility
    Odor                       : Mild
    Form                       : Free-flowing granules
    Color                      : White
    Specific Gravity           : 1.3
```

STABILITY AND REACTIVITY

Chemical Stability

    Stable at normal temperatures and storage conditions.

Conditions to Avoid

    Temperatures above 200 C (392 F) .

Incompatibility with Other Materials

    None reasonably foreseeable.

Decomposition

    HAZARDOUS DECOMPOSITION PRODUCTS - carbon monoxide and
    hydrocarbon oxidation products including organic acids,
    aldehydes and alcohols, oxides of sodium.

Polymerization

    Polymerization will not occur.

TOXICOLOGICAL INFORMATION

Animal Data

    The oral LD-50 of one type of "ELVANOL" is greater than 11000
    milligrams per kilogram of body weight as determined in rats,
    which is low toxicity.

    One type of "ELVANOL" was tested on male guinea pigs. No
    irritation or sensitization effects were noted.

    METHANOL

    Methyl Alcohol
       Oral LD50:   9,100 mg/kg in rats
       Dermal LD50   15,840 mg/kg in rabbits
       Inhalation 1 hour LC50: > 145,000 ppm in rats

    Animal testing indicates Methyl Alcohol is an eye and skin
    irritant.

    Eye contact with Methyl Alcohol caused clouding of the eye
    (corneal opacity).

    Repeated skin contact with higher concentrations of Methyl Alcohol
    caused some mortality.

    Single exposure by ingestion caused narcosis, liver effects, and
    hypothermia. Repeated exposure caused pathological changes of the
    eyes and acidosis.

    Repeated exposure by inhalation caused irritation of the eyes, and
    blindness.

    No animal data are available to define the carcinogenicity of
    Methyl Alcohol. Exposure of pregnant rats shows the following
    developmental effects: reduced birth weight, bone abnormalities,
    and behavioral abnormalities. Exposure of pregnant mice shows the
    following developmental effects: reduced birth weight, resorption,
    and bone abnormalities. No adequate animal data are available to
    define the reproductive effects of Methyl Alcohol. Tests have
    shown that Methyl Alcohol does not cause genetic damage in
    bacterial or mammalian cell cultures, or in animals. Methyl
    Alcohol has not been tested for its ability to cause permanent
    genetic damage in reproductive cells of mammals (not tested for
    heritable genetic damage).

ECOLOGICAL INFORMATION

Ecotoxicological Information

    AQUATIC TOXICITY:

    Concentrations of "ELVANOL" up to 10,000 milligrams per liter of
    water showed no mortality or other effect when tested on bluegill
    sunfish.

DISPOSAL CONSIDERATIONS

Waste Disposal

    Preferred options for disposal are (1) recycling, (2) incin-
    eration with energy recovery, and (3) landfill. The high fuel
    value of this product makes option 2 very desirable for material
    that cannot be recycled. Treatment, storage, transportation, and
    disposal must be in accordance with applicable federal,
    state/provincial, and local regulations.

TRANSPORTATION INFORMATION

Shipping Information

    DOT
    Proper Shipping Name   : Not applicable
    Hazard Class   : Not regulated

REGULATORY INFORMATION

U.S. Federal Regulations

    TSCA Inventory Status   : In compliance with TSCA Inventory
                               requirements for commercial purposes.

State Regulations (U.S.)

    STATE RIGHT-TO-KNOW

    No substances on the state hazardous substances list, for the
    states indicated below, are used in the manufacture of products on
    this Material Safety Data Sheet, with the exceptions indicated.

    SUBSTANCES ON THE PENNSYLVANIA HAZARDOUS SUBSTANCES LIST PRESENT
    AT A CONCENTRATION OF 1 % OR MORE (0.01% FOR SPECIAL HAZARDOUS
    SUBSTANCES)- Methanol.

                   (REGULATORY INFORMATION - Continued)

    WARNING - SUBSTANCES KNOWN TO THE STATE OF CALIFORNIA TO
    CAUSE CANCER, BIRTH DEFECTS OR OTHER REPRODUCTIVE HARM -
    Acetaldehyde, Ethylene oxide, Formaldehyde, Hydrazine, and
    1,4-dioxane.

    SUBSTANCES ON THE NEW JERSEY WORKPLACE HAZARDOUS SUBSTANCE
    LIST PRESENT AT A CONCENTRATION OF 1% OR MORE (0.1% FOR
    SUBSTANCES IDENTIFIED AS CARCINOGENS, MUTAGENS OR
    TERATOGENS) - Methanol.

OTHER INFORMATION

NFPA, NPCA-HMIS

    NPCA-HMIS Rating
    Health   : 1
    Flammability   : 1
    Reactivity   : 0

    Personal Protection rating to be supplied by user depending on use
    conditions.

Additional Information

    MEDICAL USE: CAUTION: Do not use in medical applications
    involving permanent implantation in the human body. "ELVANOL" is
    intended for industrial use and is expressly not for use in
    cosmetic, personal care and pharmaceutical or similar
    applications. For other medical applications see DuPont CAUTION
    Bulletin No. H-50102.

    The data in this Material Safety Data Sheet relates only to the
    specific material designated herein and does not relate to use in
    combination with any other material or in any process.

    Responsibility for MSDS : T. P. PRICE
                              DUPONT PACKAGING & INDUSTRIAL POLYMERS
    Address   : CHESTNUT RUN PLAZA 713
                              WILMINGTON, DE 19880-0713
    Telephone   : 302-999-4664

    # Indicates updated section.

 This information is based upon technical information believed to be
    reliable. It is subject to revision as additional knowledge and
                      experience is gained.

                          End of MSDS

DuPont™ Elvanol® 71-30
POLYVINYL ALCOHOL

Product Data Sheet

Description

Elvanol® 71-30 is a medium viscosity, fully hydrolyzed grade of polyvinyl alcohol. White and granular, it is soluble in hot water but insoluble in cold water and common organic solvents. For most applications, Elvanol® 71-30 is prepared in water solutions. On evaporation of water, transparent films are formed which have high tensile strength and tear resistance. The binder characteristics of Elvanol® offer excellent adhesion to porous, hydrophilic surfaces.

Typical Properties of Elvanol® 71-30	
Viscosity, cps[1]	27.0-33.0
Solution, pH	5.0-7.0
Volatiles, wt. % max.	5.0
Ash, wt. % max.[3]	0.70

[1] Viscosity in mPa.s (cP) of a 4% solids aqueous solution at 20°C (68°F)
[2] Mole percent hydrolysis of acetate groups, dry basis
[3] Dry basis, calculated as % Na_2O

Suggested Uses

Elvanol® 71-30 offers a combination of excellent film forming and binder characteristics, along with insolubility in cold water and organic solvents. This combination of characteristics is useful in a variety of applications. Elvanol® 71-30 is widely used in the paper industry at the size press and calender stack, and in adhesives tackified with boric acid.

Adhesives

In adhesive applications Elvanol®71-30 can be used alone or often in combination with extenders such as starch, dextrin or clay. As the proportion of Elvanol® increases, the adhesive strength and water resistance also improve. Examples of Elvanol® adhesives applications include:

- for paper and paperboard, alone or in combination with other additives;
- as a component in industrial adhesives for bonding paper, textiles, leather, films and porous substrates;
- for laminating adhesives which are used in the manufacture of solid fiberboard, linear board, spiral wound tubes and cores, and laminated specialties;
- in bag adhesives and pastes; and
- as an adhesive in corrugated container board.

The medium viscosity gives flexibility in formulating water based adhesives with boric acid with or without clay and/or starch.

Paper and Paperboard Sizing and Coatings

In sizing and coatings for paper and paperboard, Elvanol® 71-30 can be used alone or combined with starch and/or pigment. The proportion of Elvanol® to be used depends on desired physical properties and economics. Some specific paper uses include:

- For fine writing and printing papers as surface size material with starch;
- as grease-proof coating or release coating on paper specialties; and
- as binder in pigmented size press coatings to provide pigment loading.
- When substituted for all or part of the starch, the lower binder add-on improves opacity and makes the paper less yellow.
- Elvanol® 71-30 is easily jet-cooked alone or with starch with no additional holding time required after cooking.
- Elvanol® 71-30 has found wide use as a calender stack treatment for controlling curl and linting for paperboard grades.
- Elvanol® 71-30 is a good choice as a carrier for grease and oil-resistant treatments applied at the size press or calender stack.
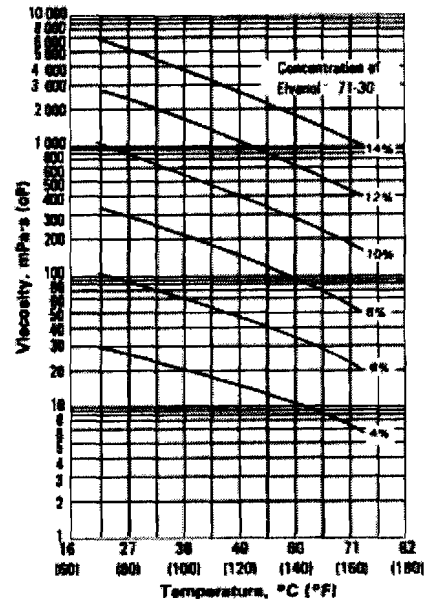
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Figure 1. Effects of Concentration on Viscosity of Elvanol® 71-30
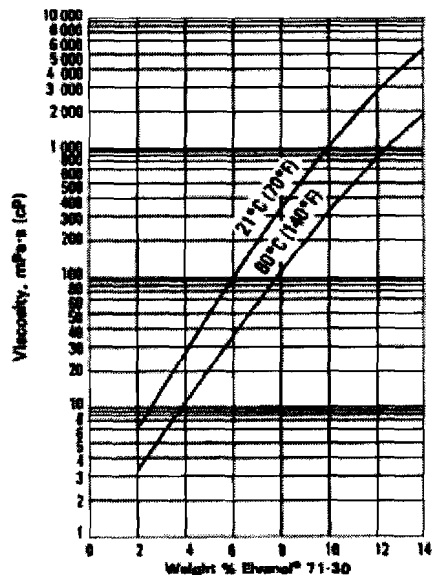
Figure2. Effects of Temperature on Viscosity of Elvanol® 71-30

Films

Unsupported films cast from water solutions of Elvanol® 71-30 and plasticizers are transparent, tough, tear-resistant and puncture-resistant. Elvanol® provides a unique combination of properties. Films have hot water solubility, in addition to resistance to oils, grease and solvents, and have low oxygen and water vapor transmission rates. These properties make films of Elvanol® 71-30 suitable for dissolvable unit packages and hospital laundry bags where hot water solubility and cold water resistance is needed.

FDA Status

Elvanol® 71-30 polyvinyl alcohol complies with U.S. Food and Drug Administration (FDA) Regulations under the following Sections of Title 21 CFR, and may be used in contact with food, subject to the limitations and requirements therein:

- 175.105 - - Adhesives.
- 175.300 - - Resinous and polymeric coatings(1)
- 175.320 - - Resinous and polymeric coatings for polyolefin films [2]
- 176.170(b) - - Components of paper and paperboard in contact with aqueous and fatty foods(3)
- 176.180 - - Components of paper and paperboard in contact with dry food(4)
- 177.1200 - - Cellophane
- 177.1670 - - Polyvinyl alcohol film(5)
- 177.2260 - - Filters, resin-bonded(6)

(1) Subject to the finished food-contact article meeting the extractive limitations under the intended conditions of use, as shown in paragraph (c).

(2) For use only as a dispersing agent at levels not to exceed 6 percent of total coating weight in coatings for polyolefin films provided the finished polyolefin films contact food only of Types V, VIII and IX (identified in 21 CFR 176.170(c), Table 1), subject to the finished food-contact article meeting the extractive limitations under the intended conditions of use, as shown in paragraph (c).

(3) Subject to the finished food-contact surface of the paper or paperboard meeting the extractive limitations under the intended conditions of use, as shown in paragraph (c) of the Regulation.

(4) As a component of the uncoated and coated food-contact surface of paper and paperboard in contact with dry food (Food Type VIII, identified in 21 CFR 176.170(c), Table 1).

(5) In the preparation of polyvinyl alcohol film that may be used in contact with food of Types V, VIII and IX (identified in 21 CFR 176.170(c), Table 1), provided the food-contact film in contact with food Types V or IX is subject to the finished food-contact surface of the paper or paperboard meeting the extractive limitations under the intended conditions of use, as shown in paragraph (b) of the Regulation. The finished food-contact film shall not be used as a component of food containers intended for use in contact with water.

(6) Subject to the finished resin-bonded filter meeting the extractive limitations under the intended conditions of use, as shown in the Regulation. In accordance with good manufacturing practice, finished filters should be thoroughly cleansed prior to their first use in contact with food.

(7) For use in textiles and textile fibers that may be used as articles or components of articles in contact with dry food (Food Type VIII, identified in 21 CFR 176.170(c), Table 1).

Safety & Handling

Read and understand the Materials Safety Data Sheet (MSDS) before using this product. Elvanol® is technical quality polyvinyl alcohol. It is not recommended for inclusion in any food or preparation that might be taken internally.

Under certain conditions of use, dust may be formed from Elvanol® polyvinyl alcohol. DuPont recommends that dust from Elvanol® be treated as a nuisance dust, which is regulated by the Occupational Safety and Health Administration (OSHA) under Title 29, Code of Federal Regulations, Section 1910.1000. Under this section, an employee's exposure to nuisance dust shall be limited to 15 milligrams per cubic meter (mg/m3) of total dust and 5 mg/m3 of respirable dust on a time-weighted average in any 8-hour shift of a 40-hour week.

The DuPont limit for polyvinyl alcohol exposure to nuisance dust is 10 mg/m3, and for respirable dust is 5 mg/m3. If excessive concentrations of dust are encountered, a mask or respirator and goggles should be worn. The mask or respirator should comply with Section 1910.134 of the OSHA regulations; the goggles should comply with Section 1910.133.

For bulk storage and handling of Elvanol® (e.g. storage silos) refer to *Elvanol® Bulk Storage and Handling Safety Guide*.

Elvanol® may be disposed of by incineration or landfill. However, any disposal method must be in compliance with all applicable local, state and federal regulations

DuPont Offices Worldwide

Americas
DuPont Company, BMP26-2363
Lancaster Pike & Route 141
Wilmington, DE 19805 U.S.A.
Telephone +1 302 774 1161
Toll-free (USA) 800 628 6208
Fax +1 302 892 7390

DuPont do Brasil, S.A.
Alameda Itapecuru, 506
06454-080 Barueri, SP Brasil
Telephone +55 11 4166 8542
Fax +55 11 4166 8720

Asia Pacific
DuPont China Holding Co, Ltd.
15th Floor, Shui on Plaza
333 Huai Hai Road (Central)
Shanghai 200021, China
Telephone +86 21 6386 6366
Fax +65 6272 7494

Europe / Middle East / Africa
DuPont de Nemours Int'l. S.A.
2, Chemin du Pavillon Box 50
CH-1218 Le Grand Saconnex
Geneva, Switzerland
Telephone +41 22 717 51 11
Fax +41 22 717 55 00

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DuPont™ Elvanol® 90-50
POLYVINYL ALCOHOL

Product Data Sheet

Description

Elvanol® 90-50 is a fully hydrolyzed polyvinyl alcohol (PVOH) designed to provide high film strength and binding power in relatively low-viscosity systems.

Typical Properties of Elvanol® 90-50	
Viscosity, cps[1]	11.6-15.4
Solution, pH	5.0-7.0
Volatiles, wt., % max.	5.0
Ash, wt. % max.[2]	0.70

[1] Viscosity in mPa.s (cP) of a 4% solids aqueous solution at 20°C (68°F)
[2] Dry basis, calculated as % Na$_2$O

Resin Characteristics

This polyvinyl alcohol provides tensile and adhesive strength approaching that of the medium viscosity, fully hydrolyzed commercial grade, Elvanol® 71-30. Elvanol® 90-50 permits higher solids solutions at a given viscosity and temperature, or lower solution viscosities at the same solids content and temperature as compared with Elvanol® 71-30.

The viscosity vs. concentration and viscosity vs. temperature characteristics of Elvanol® 90-50 are compared in Figures 1 and 2, respectively.

Figure 1. Viscosity vs. Concentration
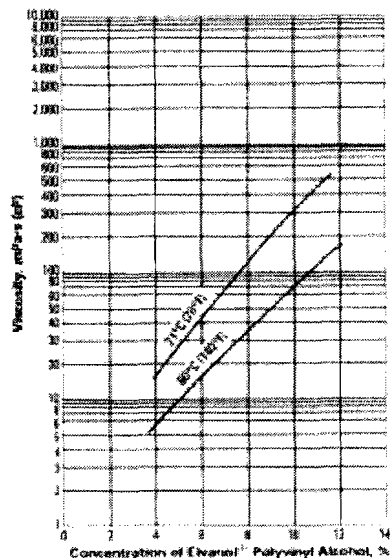
Figure 2. Viscosity vs. Temperature
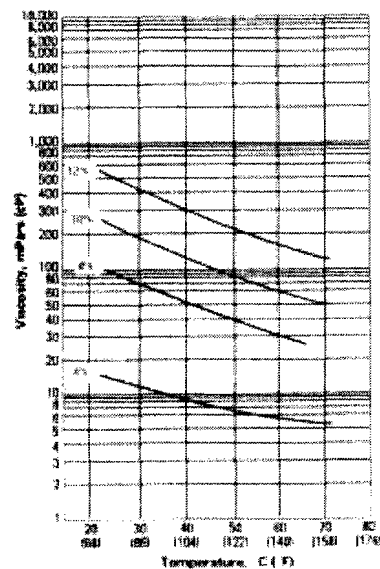
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Suggested Uses

Elvanol® 90-50 is suggested for evaluation wherever the high film strength and oil, grease, and solvent resistance associated with higher viscosity, fully hydrolyzed polyvinyl alcohols are desired, but a lower solution viscosity is needed. For example, it should be useful in such applications as paper coating and sizing, adhesives for porous substrates including paper and paperboard, hot-water-soluble film, and as a binder for pigments or other sold particles. Elvanol® 90-50 is particularly useful as a pigment binder for ceiling tile primers.

FDA Status

Elvanol® 90-50 polyvinyl alcohol complies with U.S. Food and Drug Administration (FDA) Regulations under the following Sections of Title 21 CFR, and may be used in contact with food, subject to the limitations and requirements therein:

- 175.105 - Adhesives
- 175.300 - Resinous and polymeric coatings [1]
- 175.320 - Resinous and polymeric coatings for polyolefin films [2]
- 176.170(b) - Components of paper and paperboard in contact with aqueous and fatty foods [3]
- 176.180 - Components of paper and paperboard in contact with dry food [4]
- 177.1200 - Cellophane
- 177.1670 - Polyvinyl alcohol film [5]
- 177.2260 - Filters, resin-bonded [6]
- 177.2800 - Textiles and textile fibers [7]

(1) Subject to the finished food-contact article meeting the extractive limitations under the intended conditions of use, as shown in paragraph (c).

(2) For use only as a dispersing agent at levels not to exceed 6 percent of total coating weight in coatings for polyolefin films provided the finished polyolefin films contact food only of Types V, VII and IX (identified in 21 CFR 176.170(c), Table 1), subject to the finished food-contact article meeting the extractive limitations under the intended conditions of use, as shown in paragraph (c).

(3) Subject to the finished food-contact surface of the paper or paperboard meeting the extractive limitations under the intended conditions of use, as shown in paragraph (c) of the Regulation.

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(6) Subject to the finished resin-bonded filter meeting the extractive limitations under the intended conditions of use, as shown in the Regulation. In accordance with good manufacturing practice, finished filters should be thoroughly cleansed prior to their first use in contact with food.

(7) For use in textiles and textile fibers that may be used as articles or components of articles in contact with dry food (Food Type VIII, identified in 21 CFR 176.170(c), Table 1).

Safety & Handling

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The DuPont limit for polyvinyl alcohol exposure to nuisance dust is 10 mg/m3, and for respirable dust is 5 mg/m3. If excessive concentrations of dust are encountered, a mask or respirator and goggles should be worn. The mask or respirator should comply with Section 1910.134 of the OSHA regulations; the goggles should comply with Section 1910.133.

For bulk storage and handling of Elvanol® (e.g. storage silos) refer to *Elvanol® Bulk Storage and Handling Safety Guide.*

Elvanol® may be disposed of by incineration or landfill. However, any disposal method must be in compliance with all applicable local, state and federal regulations.

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Wilmington, DE 19805 U.S.A.
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Toll-free (USA) 800 628 6208
Fax +1 302 892 7390

DuPont do Brasil, S.A.
Alameda Itapecuru, 506
06454-080 Barueri, SP Brasil
Telephone +55 11 4166 8542
Fax +55 11 4166 8720

Asia Pacific
DuPont China Holding Co, Ltd.
15th Floor, Shui on Plaza
333 Huai Hai Road (Central)
Shanghai 200021, China
Telephone +86 21 6386 6366
Fax +65 6272 7494

Europe / Middle East / Africa
DuPont de Nemours Int'l. S.A.
2, Chemin du Pavillon Box 50
CH-1218 Le Grand Saconnex
Geneva, Switzerland
Telephone +41 22 717 51 11
Fax +41 22 717 55 00

Elvanol.dupont.com

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